MECHANISTIC AND REACTIVITY STUDIES OF BENT METALLOCENE COMPLEXES OF NIOBIUM AND TANTALUM

Thesis by

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Science has become so complicated that it is impossible for a single person to be able to accomplish much without the help of a great many other people. Caltech has certainly provided an open and friendly environment in which to learn. The interactions that are fostered here between students and faculty (even visiting professors and professionals) have lead to a very enriching experience.

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ABSTRACT

A variety of olefin hydride complexes of niobium and tantalum has been prepared in order to study their reactivity and to gain insight into organometallic reaction mechanisms. Examination of a series of ethylene and propylene complexes of niobocene (Cp_2Nb; Cp = η^5–C_5H_5), permethylniobocene (Cp^*_2Nb; Cp* = η^5–$C_5(CH_3)_5$), tantalocene, and permethyltantalocene has indicated that there are both large electronic and steric effects deriving from the metal (and its ancillary ligands) in the olefin insertion (β-migratory insertion) process. Furthermore, a thermodynamic and kinetic analysis has been completed for a series of substituted styrene complexes of niobocene in order to better understand the important electronic properties of the olefin. The results are in accord with a concerted four-center process with only moderate charge development.

The special case of β-migratory insertion of a hydride ligand into coordinated benzyne has also been studied for the permethyltantalocene system. The coordinatively unsaturated (sixteen electron) phenyl tautomer, which is made accessible by the facile benzyne hydride insertion reaction, readily reacts with a variety of ligands, L, to afford $Cp^*_2Ta(C_6H_5)L$ complexes (L = CO, O_2, NC≡R, $:CH_2$, H_2, *etc.*). This family of compounds exhibits interesting reactivity (α-migratory insertion, O_2 activation, and reductive elimination) which is discussed in some detail.

Finally a series of paramagnetic seventeen electron $Cp^*_2TaX_2$ (X = halide, alkyl, hydride) complexes, and the corresponding cationic and anionic species, have been prepared and studied. The odd electron neutral complexes exhibit surprising thermal stability and undergo very little reactivity. While the chemistry of the anionic compounds is almost completely dominated by their potent reducing power, that of the cations is quite diverse and amenable for study. Therefore the syntheses and reactivity (1,2-eliminations, ligand insertions, and deprotonation reactions) of these coordinatively unsaturated sixteen electron species are presented.

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ABBREVIATIONS

Anal.	elemental analysis
br	broad
Calcd.	calculated
cmpd	compound
Cp	η-C_5H_5
Cp^{ϕ}	η^5–$C_5(CH_3)_4(C_6H_5)$
Cp*	η^5–$C_5(CH_3)_5$
d	doublet
Et	C_2H_5
imp	impurity
IR	Infrared spectroscopy
m	multiplet
Me	CH_3
MT	magnetization transfer
NMR	Nuclear Magnetic Resonance spectroscopy
Ph	C_6H_5
Pr	propyl
quin	quintet
s	singlet
t	triplet
≈t	pseudotriplet (in describing NMR coupling patterns)

INTRODUCTION

Although the first organotransition-metal complex ($[K][Cl_3Pt(C_2H_4)]$, Zeise's salt) was discovered in the early 1800's, the field of organometallic chemistry received very little attention until the 1900's with the advent of metal catalyzed industrial processes such as Fischer-Tropsch, the oxo process, and homogeneous hydrogenation. Even so, little fundamental knowledge of organometallic compounds was attained until the 1950's with the elucidation of the correct structure of ferrocene. It was also during this period that Ziegler-Natta polymerization of olefins was discovered thus fueling intense interest in the field.[1] Organometallic chemistry is no longer that young discipline of thirty or forty years ago. Indeed with the rapid development of techniques such as NMR spectroscopy,[2] X-ray crystallography,[3] and the many elegant methods for the manipulation of air sensitive materials,[4] the number of novel organometallic compounds has grown explosively. Although the field may be approaching a degree of maturity, there are still many fundamental processes and phenomena that are not very well understood and a host of new areas to which organometallic expertise could be applied.[5]

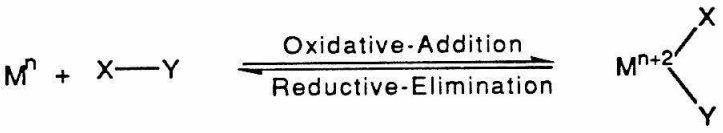
Since organotransition-metal chemistry to some extent owes its existence to the wide variety of industrial catalysis that it supports, it is logical to expect that mechanistic analysis should be an important aspect of the area. It is a difficult task to attempt to design and modify relatively complex catalytic systems without having guiding principles. Mechanistic studies have been pursued[6] but the set of transition metals presents a high degree of variability, much more so than does a carbon atom. The presence of the metal can also affect the reactivity of the organic ligands so that the rules derived from organic chemistry may or may not apply. Therefore obtaining a detailed understanding of organometallic chemistry can be even more challenging than for organic chemistry.

Those transformations of organometallic chemistry that must be considered the most fundamental are summarized in Scheme 1. Reactions categorized as addition / elimination are,

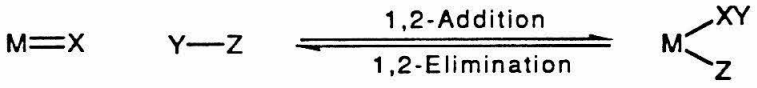
SCHEME 1

Fundamental Organometallic Reactions

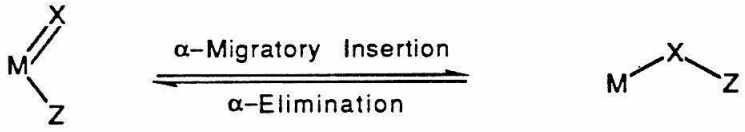
Oxidative Addition / Reductive Elimination

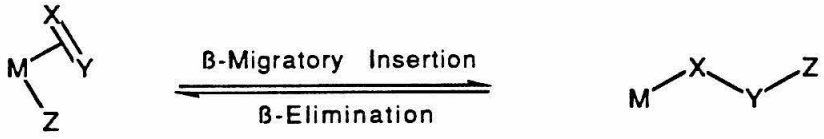


1,2-Addition / Elimination



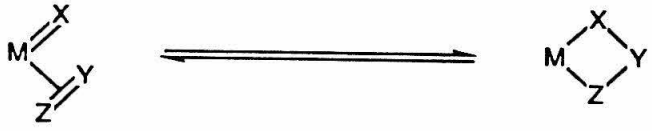
Migratory Insertion / Elimination





Attack on Coordinated Ligand

Ligand Coupling Reactions



most obviously, ways of getting substrates onto and products off of catalyst molecules. As such, these types of processes are often proposed as initiation and termination steps for a variety of catalytic cycles. An entire spectrum of mechanisms have been found for even the most "simple" subset of this class of reactions, oxidative-addition / reductive-elimination.[7] For instance, there are actually only a very few cases for which straightforward reductive-elimination can be studied in any detail, thus it would be of great scientific interest to examine such a system. Other types of eliminations can involve more subtle changes at the metal (*e.g.*, a change in the coordination environment but not necessarily the formal oxidation state as in 1,2-eliminations) and these also require further mechanistic study.

Migratory insertion / elimination reactions can occur for a variety of ligand types, two of the major classifications of which are depicted in Scheme 1. In many cases (*e.g.*, polymerization and hydroformylation), these are the reactions in a catalytic cycle that can be considered to be effecting the desired transformation (the propagation steps). Of course, these processes can also serve as initiation/termination, for instance the direct insertion of olefin into metal hydride or alkyl bonds. It would be of interest to understand these reactions on a very fundamental level so as to have some guiding principles for the design and modification of catalyst systems.

The aim of this thesis work had been to prepare transition metal compounds to be used for the study of certain fundamental organometallic transformations: migratory-insertion and reductive-elimination reactions in particular but not exclusively. The Group V metallocenes were chosen as an optimal system for such studies for a wide variety of reasons. First of all as implied by terms like oxidative addition and reductive elimination, some of the processes that we wish to study involve a formal change of oxidation state of the metal atom. β-migratory insertion reactions for metal olefin complexes can also be considered to involve oxidation state changes if the bonding involved a high degree of metallacyclopropane character (*cf.* Chapter 1).[8] Niobocene and tantalocene complexes are common in only the +3, +4, and +5 oxidation

states, giving these systems the limited flexibility needed for the desired studies. Also of importance to the olefin insertion studies was the observation that isolable olefin hydride complexes existed and exhibited reversible migratory insertion/elimination reactions.[9]

The geometries, electron counts, and molecular orbital picture[10] of these metallocenes also seemed to be well suited for these studies. The niobocene and tantalocene fragments have three orbitals available for bonding and electron counts of fifteen. Therefore, complexes with up to 3 one-electron ligands (alkyls, hydrides, *etc.*) or 1 one-electron and 1 two-electron ligands (*e.g.* olefin hydride complexes) can be formed. Conveniently all three frontier orbitals for these fragments lie in the plane (or the "wedge") between the two cyclopentadienyl rings. Aside from enforcing a *cis*-arrangement of the ligands of interest, the fact that there are no accessible orbitals out of the wedge (and likely also due to steric interactions with the Cp rings) prevents complications such as olefin rotations.

Chapter 1 will describe kinetic studies of the β-migratory insertion reaction into coordinated olefin. This process was studied by varying the metal, the ancillary ligands on the metal, and the substituents on the olefin. The results of these experiments help provide some insight into the various steric and electronic effects that are in play in the olefin insertion reaction. Chapter 2 begins as an extension of this work, with examination of β-hydrogen insertion into the special ligand, benzyne. The insertion reaction makes a coordinatively unsaturated phenyl complex available which can be derivatized into many kinds of new compounds. A large part of the remainder of Chapter 2 is devoted to summarizing the chemistry of some of the more interesting examples of this family of compounds.

Finally in Chapter 3, we wander completely away from β-migratory processes and are primarily interested in synthesizing some new compounds and surveying their reactivity. In particular, it had been initially hoped that cationic or anionic alkyl complexes could be prepared that could subsequently be transformed into alkyl hydride species. Such compounds were desired for studies of reductive elimination reactions but, ultimately, a different type of reactivity

was observed: 1,2-elimination. The chemistry of the charged alkyl complexes will be discussed with regard to 1,2-elimination, insertion, and acid-base reactivity.

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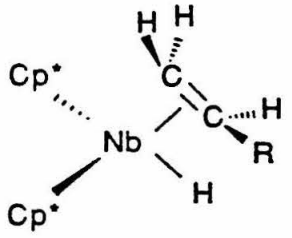
CHAPTER 1

Kinetics and Mechanism of the Insertion of Olefins into Niobium and Tantalum Hydride Bonds: A Study of the Competition between Steric and Electronic Effects.

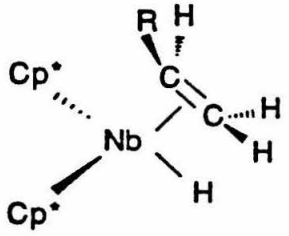
Abstract: The mechanism of insertion of olefins into transition metal hydride bonds has been examined for a series of olefin hydride complexes of niobocene, permethylniobocene, tantalocene, and permethyltantalocene. A comparison of the rates for the entire series of ethylene compounds (where steric effects are minimal) indicates that there are significant electronic effects acting within this family ($k_{Nb} > k_{Ta}$ and $k_{Cp} > k_{Cp^*}$; Cp = (η^5-C_5H_5), Cp* = (η^5-C_5Me_5)). In contrast to the pentamethylcyclopentadienyl systems for which steric interactions appear to dominate, the normal cyclopentadienyl compounds are virtually insensitive to sterics, allowing for the existence of two isomeric forms of the α-olefin hydride complexes (*endo*, olefin substituent central, and *exo*, olefin substituent lateral in the equatorial plane) in roughly 1:1 proportion. The series of propylene hydride compounds, while showing some electronic effects ($k_{Nb} > k_{Ta}$), further demonstrates the importance of steric interactions in determining the rates of olefin insertion ($k_{Cp^*} > k_{Cp}$). A thermodynamic and kinetic analysis has been completed for a series of niobocene styrene hydride complexes to better define the electronic requirements for the [(η^5-C_5H_5)$_2$Nb] derivatives, a system where the interfering steric interactions are minimized. The ground state orderings (ΔG^0) are strongly dependent upon the *para*-substituent (ρ = +2.2). The insertion rates for the *endo* and *exo* forms are also dependent on the substitution of the phenyl ring, and ρ values of -1.1 and +0.7, respectively, have been measured. These results are interpreted in terms of a concerted four-center model with moderate positive charge buildup at the β-carbon and, in the case of the *endo* isomer, competing ground and transition state effects.

INTRODUCTION

Olefin insertion into metal hydrogen bonds and its microscopic reverse, β-H elimination, are very common reactions in organometallic chemistry, yet few mechanistic studies of these fundamental transformations have been carried out.[1,2] Previous investigations have focused on the first of these transformations, olefin insertion into Nb-H bonds, and a series of olefin hydride complexes of permethylniobocene, $Cp^*_2Nb(CH_2=CHR)H$ ($Cp^* = \eta^5$-C_5Me_5; R = H, Me, Ph, C_6H_4-*m,p*-X (X = CF_3, Me, OMe, NMe_2)) has been examined.[2] Even where R ≠ H, a single isomer is formed, which from NMR data[2b], steric considerations, and an X-ray crystal determination[2c,d] was shown to be that with the olefin substituent R located at the *endo* (central, less crowded) position of the equatorial plane of the bent sandwich structure.



endo



exo

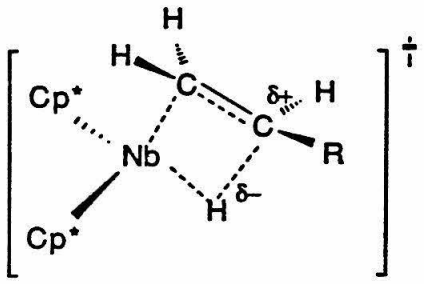
Insertion of olefins into niobocene hydride bonds (k_1) is reversible, and a lower limit for k_{-1} (>100 k_1) can be estimated (equation 1) from the undetectably small concentrations (^{1}H NMR) of the alkyl tautomer.

$$Cp^*_2Nb(CH_2=CHR)H \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Cp^*_2Nb\text{-}CH_2CH_2R] \xrightarrow[L]{k_2} Cp^*_2Nb(CH_2CH_2R)L \qquad (1)$$

Interception of the coordinatively unsaturated intermediate by an external ligand (L = CO, $CNCH_3$) is much slower than β-H elimination, so that the rate of formation of $Cp^*_2Nb(CH_2CH_2R)L$ follows second order kinetics, first order in both $[Cp^*_2Nb(CH_2=CHR)H]$ and

[L], even at the highest practical concentrations of trapping ligand, L. Thus, values for the k_1's in equation 1 were not directly obtainable from kinetics of these ligand trapping experiments.

The rates of insertion of olefins into the Nb-H bond (k_1) were, however, determined by magnetization transfer and coalescence techniques (^{1}H NMR), and a model for the insertion process for the permethylniobocene system has been developed: olefin insertion proceeds *via* a four center transition state with partial positive charge development at the β-carbon of the incipient metal alkyl.[3]



Electronic effects on the ground states of $Cp^*_2Nb(CH_2{=}CHC_6H_4$-*m,p*-X)H were found to be small, but a modest effect on the relative transition state energies is evident from the differing rates of olefin insertion for various substituted styrenes. Electronic effects can be transmitted either through the σ framework (induction) or the styrene π system (resonance). An approximate measure of the relative contributions of these two different modes of transmission can be gained through a comparative study of the rates of insertion for *meta*- and *para*-substituted styrenes. *Meta*-substituent effects on the reaction rate are transmitted principally through induction, whereas combined resonant and inductive effects operate for the *para*-substituted styrenes.[4] Such experiments indicated that the electronic effects are largely inductive in nature for the permethylniobocene system. In addition, a crystal structure determination of the parent styrene hydride complex, $Cp^*_2Nb(CH_2{=}CHC_6H_5)H$ was carried out and verified that the phenyl ring was twisted out-of-resonance with the olefin π-system, thus likely attenuating any resonance substituent effects, at least in the ground state.[2b,d]

In view of the relatively large steric effects established for the permethylniobocene system by these studies, it was of interest to undertake a complementary study of the olefin insertion process in a system where steric considerations would be greatly diminished. Electronic effects are more easily probed when interfering steric effects are minimized. Moreover, the substitution of (η^5-C_5H_5) for the bulkier (η^5-C_5Me_5) rings also permitted the ancillary ligand electronic effects to be examined. For example, to the extent that the olefin hydride complex is formally Nb^V (considering the metal-olefin bonding in the niobacyclopropane limit) and the insertion product is formally Nb^{III}, the more electron-releasing (η^5-C_5Me_5) ligands might be expected to exhibit slower rates of olefin insertion due to stabilization of the ground state relative to the transition state, the latter more closely resembling the insertion product according to the Hammond postulate[5]. Interestingly, the steric and electronic effects of methyl substitution of the two cyclopentadienyl rings are predicted to operate in opposite directions, since sterically demanding pentamethylcyclopentadienyl ligands should destabilize the more crowded ground state relative to the transition state. Thus, such a comparative study of [Cp_2Nb] *vs.* [Cp^*_2Nb] should allow the relative importance of electronic and steric effects to be determined.

Accordingly, a series of olefin hydride complexes of bis(cyclopentadienyl)niobium, $Cp_2Nb(CH_2{=}CHR)H$ (Cp = (η^5-C_5H_5); R = H, CH_3, C_6H_5, C_6H_4-*p*-X, (X = CF_3, OMe, NMe_2)), has been prepared. Some of these niobocene olefin hydride derivatives have been previously described[6] and exist as nearly equal proportions of the *endo* and *exo* isomers, presumably due to reduced steric demands in these systems. The relative ground state energies and rates of olefin insertion for these complexes have been measured for comparison to the permethylniobocene system. Since a synthetic entry into olefin hydride derivatives of permethyltantalocene[7] has recently been developed, the measurement of olefin insertion rates for these complexes and their tantalocene congeners synthesized previously[6b,d] has also been undertaken to provide quantitative differences in rates between analogous compounds for members of the second and third row of the Group 5 triad. Herein are reported the results of

studies of the kinetics for olefin insertion for $Cp_2Nb(CH_2{=}CHC_6H_4\text{-}p\text{-}X)H$ (X = CF_3, H, OMe, NMe_2), $Cp_2Nb(CH_2{=}CHR)H$, $Cp^*_2Ta(CH_2{=}CHR)H$ and $Cp_2Ta(CH_2{=}CHR)H$ (R = H, CH_3).

RESULTS

Synthesis and Characterization of *para*-Substituted Styrene Hydride Complexes of Niobocene. Treatment of Cp_2NbH_3 (**1**) with an excess (5 to 6 equivalents) of the appropriate *para*-substituted styrene in toluene proceeds overnight (12-24 hrs) at 25°C (in contrast to the permethylniobocene complexes which required heating to 80°C for the reaction to proceed) to afford the styrene hydride complexes **2-5**. One equivalent of the corresponding phenylethane, $p\text{-}X\text{-}C_6H_4CH_2CH_3$, is formed concomitantly. Microcrystalline yellow or green products are obtained in 50-90% yield upon addition of petroleum ether to the reaction mixture.

$$Cp_2NbH_3 + 2\,p\text{-}X\text{-}C_6H_4CH{=}CH_2 \xrightarrow[25\,^\circ C]{\text{toluene}} Cp_2Nb(CH_2{=}CHC_6H_4\text{-}p\text{-}X)H + p\text{-}X\text{-}C_6H_4CH_2CH_3 \quad \textbf{(2)}$$

X = H, CF_3, OMe, NMe_2
2 3 4 5

The product in each case is a mixture of *endo* and *exo* isomers in almost equal proportions. Although the isomers have proven to be inseparable by physical means, assignment of the ^1H NMR resonances (Table 1) of a mixture of the isomers was accomplished through difference NOE and magnetization transfer experiments (Table 2). Difference NOE experiments allowed the correlation of each of the cyclopentadienyl signals with its neighboring vinylic and hydride signals (the phenyl resonances were not well enough resolved to make definite assignments). The magnetization transfer results were then used to unambiguously assign the vinylic and hydride resonances: in the *exo* isomers the signals for the $=CH_2$ and Nb-*H* protons exhibit exchange, whereas in the *endo* isomers the $=CH(p\text{-}X\text{-}C_6H_4)$ and Nb-*H* protons undergo magnetization transfer.

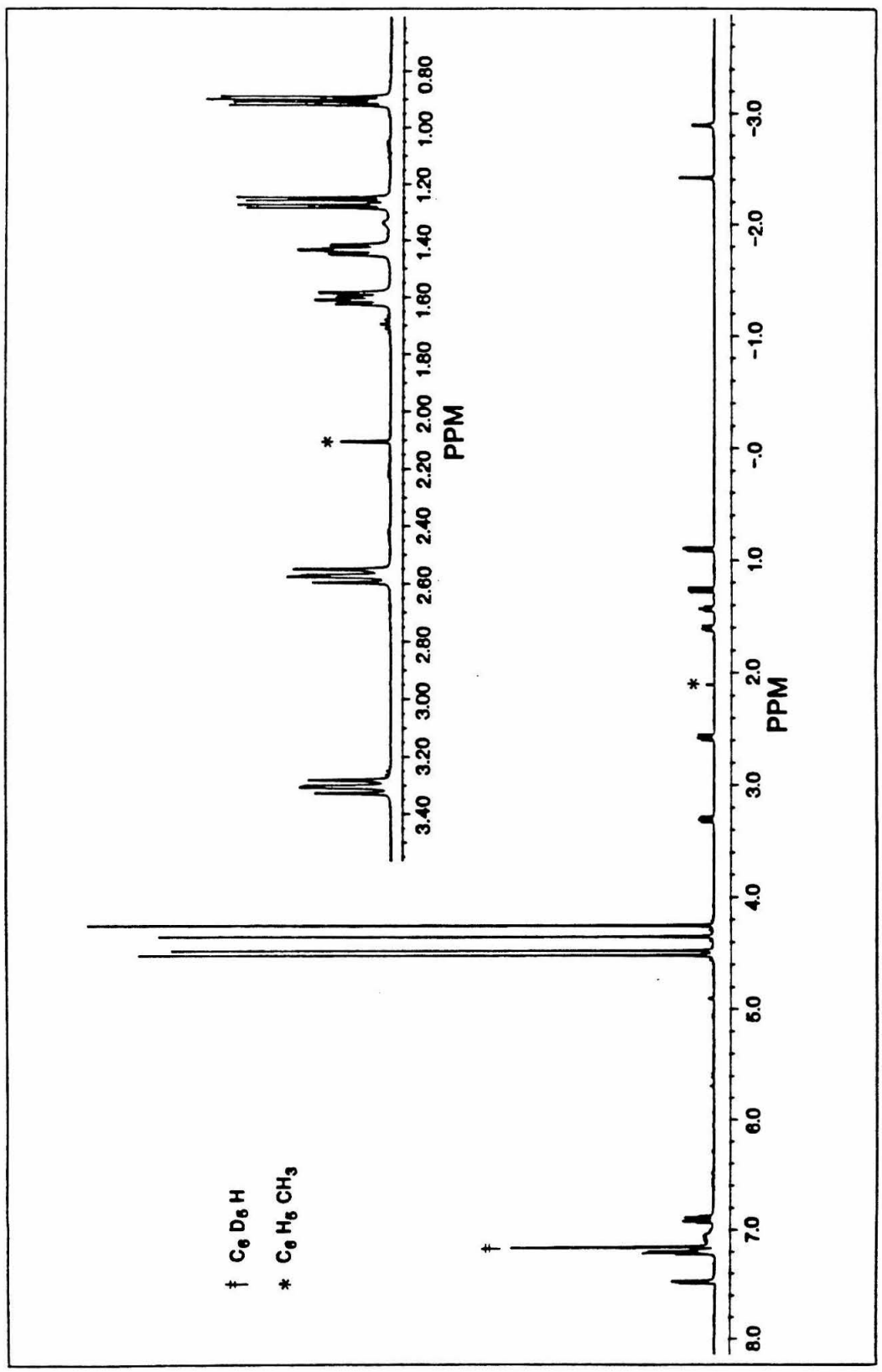


Figure 1. ^1H NMR spectrum of *exo*- and *endo*-$Cp_2Nb(H_2C{=}CHC_6H_5)H$ (non-equilibrium mixture of isomers).

Table II. Assignment of the niobocene styrene hydride isomers by NMR spectroscopy.

Difference NOE Experiments:

signal irradiated	signals showing enhancement
Cp (*endo*)	Ph, H(*endo*), H_a(*endo*)
Cp'(*endo*)	H_b(*endo*), H_x(*endo*), H(*endo*)
Cp (*exo*)	Ph, H(*exo*), H_a(*exo*)
Cp'(*exo*)	H_b(*exo*), H_x(*exo*), H(*exo*)

Magnetization Transfer Experiments:

signal irradiated	signal affected
H(*endo*)	=C*H*Ph(*endo*)
H(*exo*)	=CH_2(*exo*)

The ^{1}H NMR spectra of these niobocene complexes (see Table I and Figure 1) are similar to those of their permethylniobocene analogs. At room temperature, the inequivalent Cp rings give rise to two overlapping pairs of singlets, the signals due to the *endo* isomer being in between the two signals due to the *exo* isomer. At 500 MHz the olefinic protons of the *endo* isomer exist as three sets of doublets of doublets. The =C*H*R resonance of the *exo* complexes is likewise a doublet of doublets, but the =CH_2 protons show an additional small coupling to the Nb-*H* (J $\approx$ 2 Hz). The coupling constants of the olefinic protons are essentially independent of the *para* substitution, but the geminal coupling constant is consistently different for the *exo* ($\approx$6.8 Hz) and *endo* ($\approx$5.5 Hz) isomers. The hydride resonances are broad singlets at about -2.5 to -3.0 ppm, the signal due to the *exo* isomer always being slightly more upfield. The resonances were too broad to detect the coupling to the vinylic protons.

The feature of most interest in the ^{13}C spectra for these compounds, $^1J_{C\text{-}H}$ for the vinylic signals, is in the 145-150 Hz range, indicative of substantial metallacyclopropane character (although not quite as much as was found for the more electron-rich Cp*$_2$Nb system ($^1J_{C\text{-}H} \approx$ 140-145 Hz), as would be expected on the basis of the relative electron donating abilities of Cp and Cp*), similar to other complexes of d^2 bent metallocenes.[2,6,8] Infrared and mass spectral data are summarized in the Experimental Section.

Reactions of Olefin Hydride Compounds with Trapping Ligands. The sterically encumbered permethylniobocene olefin hydride compounds were found to react only with small ligands (L = CO and $CNCH_3$) to afford the ligand-trapped alkyl complexes $Cp^*_2Nb(CH_2CH_2R)L$. In contrast, the niobocene complexes react with a larger variety of ligands (L = CO, $CNCH_3$, PMe_3, $P(OMe)_3$, and C_2H_4); however, the predominant products (>90%) arise from substitution of the olefin by the trapping ligands to afford the previously described $Cp_2Nb(H)(L)$ compounds (L = CO[6a], PMe_3[6a], $P(OMe)_3$[9], and C_2H_4[10]). The reaction with $CNCH_3$ is more complex; there appears to be further reaction of the initial reaction product with excess methylisocyanide. Indeed, it was subsequently found that Cp_2NbH_3 reacts with excess $CNCH_3$ in a closed vessel to give high yields of $Cp_2Nb(CNCH_3)(NMe_2)$. Presumably there is an initial substitution of methylisocyanide for H_2 to afford an unobserved $Cp_2Nb(H)(CNCH_3)$ species[11] that rapidly reacts with the released hydrogen to form an amide complex that is trapped by another equivalent of $CNCH_3$ to afford the final amide-isocyanide complex.

The permethyltantalocene complexes have been shown to exhibit the same types of steric restrictions found in the permethylniobocene system[7], as may be expected on the basis of the very similar sizes of Nb and Ta. The tantalocene compounds are more stable than their niobocene analogs and have previously been shown to react with several ligands to form the trapped alkyl species.[12] We have also found that the tantalocene ethylene hydride complex will react with ethylene at elevated temperatures to form the ethylene ethyl complex. This compound has been characterized by proton NMR and found to be similar to the previously described niobocene ethylene ethyl complex.[6a,8a]

Determination of Ground State Orderings By Competitive Binding Studies. The relative ground state orderings for the niobocene olefin complexes were determined by carrying out competitive binding experiments:

$$[Nb](CH_2{=}CHC_6H_4\text{-}X)H + CH_2{=}CHR \underset{25\,^\circ C}{\overset{K_{eq}}{\rightleftharpoons}} [Nb](CH_2{=}CHR)H + CH_2{=}CHC_6H_4\text{-}X \qquad (3)$$

$$[Nb] = Cp_2Nb;\ X = H,\ p\text{-}CF_3,\ p\text{-}OCH_3,\ p\text{-}NMe_2;\ R = C_6H_5,\ CH_3$$

For the *meta*- and *para*-substituted styrene-hydride complexes of permethylniobocene[2], these experiments were performed by equilibrating the substituted olefin hydride complexes with ethylene. Equilibration *vs.* ethylene proved unsatisfactory for the normal cyclopentadienyl analogs, since the parent ethylene hydride complex reacts further with excess ethylene[6a]. Thus, the ground state position for $(\eta^5\text{-}C_5H_5)_2Nb(CH_2{=}CH_2)H$ relative to the other olefin hydride derivatives could not be determined. Performing the equilibrations of the other olefin hydride complexes (*endo*- and *exo*-**7**-**10** and *endo*- and *exo*-**16**) with styrene results in fairly complicated ^1H NMR spectra for these mixtures, but separation of the signals at 500 MHz is sufficient to allow the desired equilibrium data to be determined. The equilibrations were approached from both sides of equation 4 and converged to a single value in each case. In order to avoid decomposition and olefin polymerization, these measurements were carried out at 25°C, even though the reactions required 2-4 weeks to come to completion.

Importantly, the equilibrium *endo*:*exo* isomer ratios for the $Cp_2Nb(CH_2{=}CHR)H$ compounds are found to be insensitive to the nature of the olefin substituent, consistently 1.2 - 1.4 ($\Delta\Delta G^o$ = 0.1 - 0.2 kcal·mol^{-1}), slightly in favor of the *endo* isomer. The results of these experiments are summarized in Table III, the reported K_{eq} actually being the average of K_{eq}(*endo*) and K_{eq}(*exo*). It can be readily seen that a sizable ground state effect is operating for the [Cp_2Nb] styrene hydride complexes, much larger than observed for the [Cp^*_2Nb] system. Hammett plots (see Figure 2) of log K_{eq} show a correlation (R = 1.000) with σ_{para} with a $\rho \approx$ +2.2; whereas the fit with σ_+ is significantly poorer. In assessing the relative binding abilities for the various olefins it is necessary to account for the free energies of the uncoordinated olefins. Since these olefin complexes appear to have a high degree of metallacyclopropane character (*vide supra*), complexation to a metal center resembles hydrogenation. Assuming the olefin complexes to be roughly halfway between the metal-olefin and metallacyclopropane limiting forms and thus applying half of the free energy of hydrogenation as a correction factor as in the previously adopted manner[2b], the relative ground state orderings listed in the last column of Table III were derived. Including the free energies of hydrogenation probably affects only the

values for the propene binding constant, since the differences in heats of hydrogenation among the various substituted styrenes are likely to be small relative to the experimental error in K_{eq}.

Table III. Relative ground state energies of niobocene olefin hydrides

$Cp_2Nb(H_2C{=}CHC_6H_5)H + H_2C{=}CHR \underset{}{\overset{K_{eq},\ 25\,^\circ C}{\rightleftharpoons}} Cp_2Nb(H_2C{=}CHR)H + H_2C{=}CHC_6H_5$

R		σ_p	K_{eq} [a]	log(K_{eq})	$\Delta\Delta G^{o}$ [b]	rel GSE [b]
p-C_6H_4-CF_3	(3)	0.54	17(2)	1.230(50)	-1.7(1)	-1.7(1)
C_6H_5	(2)	0.00	1.0	0.00	0.0	0.0
p-C_6H_4-OMe	(4)	-0.27	0.29(4)	-0.544(60)	0.74(8)	0.74(8)
p-C_6H_4-NMe_2	(5)	-0.60	0.05(1)	-1.322(70)	1.8(1)	1.8(1)
CH_3	(11)	———	0.0030(5)	———	3.4(4)	3.7(4)

[a] Average of K_{eq}(*endo*) + K_{eq}(*exo*). See text for explanation. [b] Reported in kcal·mol^{-1}.

Determination of the Olefin Insertion Rate by Coalescence and Magnetization Transfer Techniques. The rates of olefin insertion (k_1) for *endo*-$Cp_2Nb(CH_2{=}CHCH_3)H$ (**11**), for *endo*-$Cp^*_2Ta(CH_2{=}CHCH_3)H$ (**12**), and for *endo*-$Cp_2Ta(CH_2{=}CHCH_3)H$ (**13**) were determined in a straightforward fashion using coalescence techniques (^{1}H NMR, 90 MHz). All of these propene hydride complexes have inequivalent Cp (C_5R_5; R = H, CH_3) rings due to the unsymmetrical substitution of the olefin (*e.g.*, *endo A* in Scheme 1 or *exo A* in Scheme 2). As further illustrated in Scheme 1 the two cyclopentadienyl ring environments for the *endo* isomers can be interchanged by olefin insertion to *A1*, rotation about the C-C single bond of the alkyl to afford *A1'*, followed by β-H elimination to *endo A'*. The rate of insertion (k_1^{endo} at the temperature of coalescence, T_c) may be calculated from the frequency separation of the two C_5R_5 resonances in the slow exchange limit[13], and the free energy of activation ($\Delta G^{\ddagger}(T_c)$) obtained from the Eyring equation. Using the cyclopentadienyl ring coalescence data, the insertion rate constants (k_1^{endo}) and activation free energies for *endo* **11-13** were obtained (Table IV).

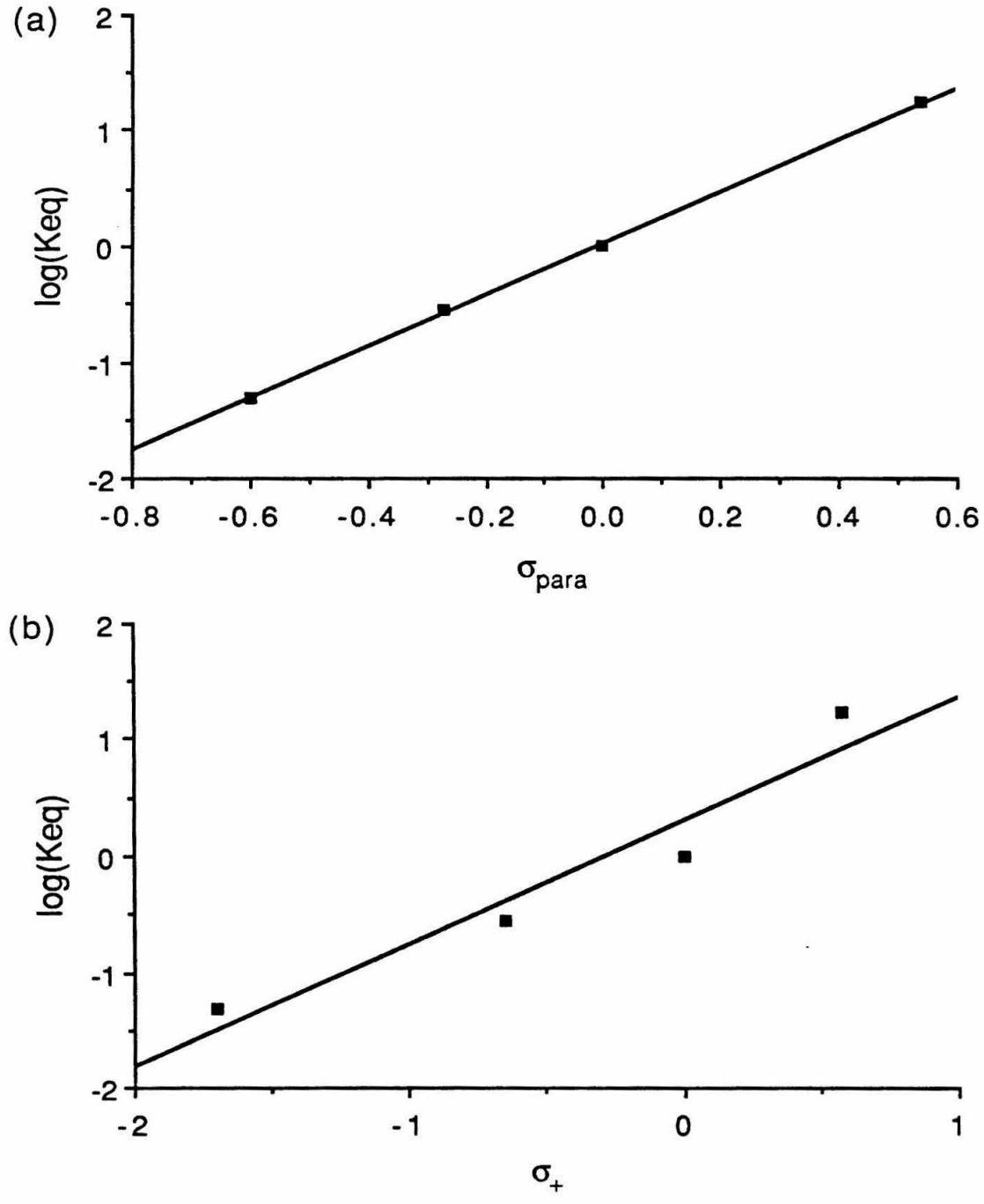
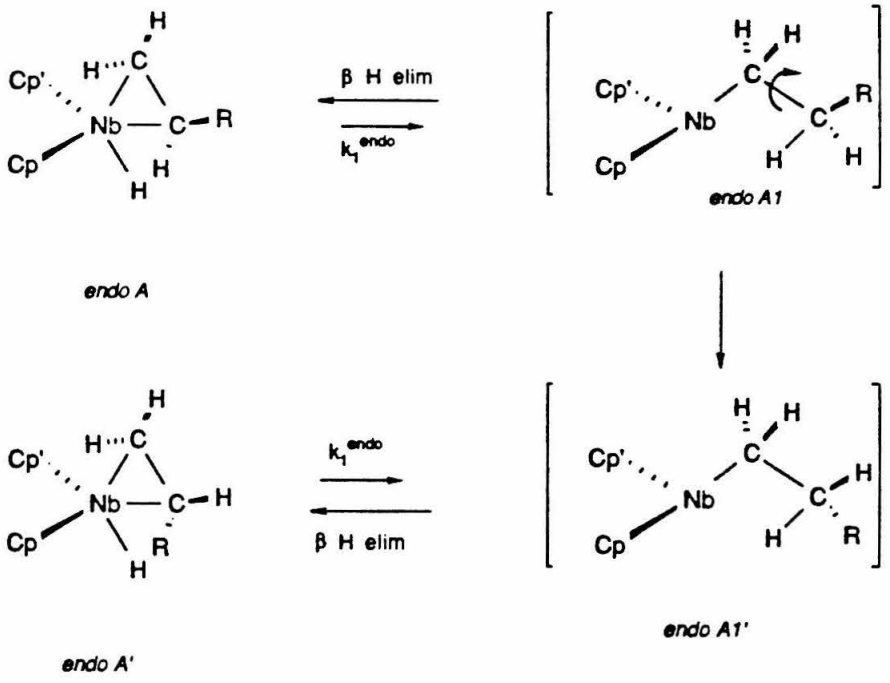


Figure 2. Hammett plot of equilibrium data for *exo*- and *endo*-$Cp_2Nb(H_2C{=}CHC_6H_4\text{-}p\text{-}X)H$ complexes (error bars are on the order of the size of the points): (a) plot of $\log(K_{eq})$ *vs.* σ_p (ρ = 2.2, R = 1.000). (b) plot of $\log(K_{eq})$ *vs.* σ_+ (ρ_+ = 1.1, R = 0.964).

Scheme 1



Scheme 2

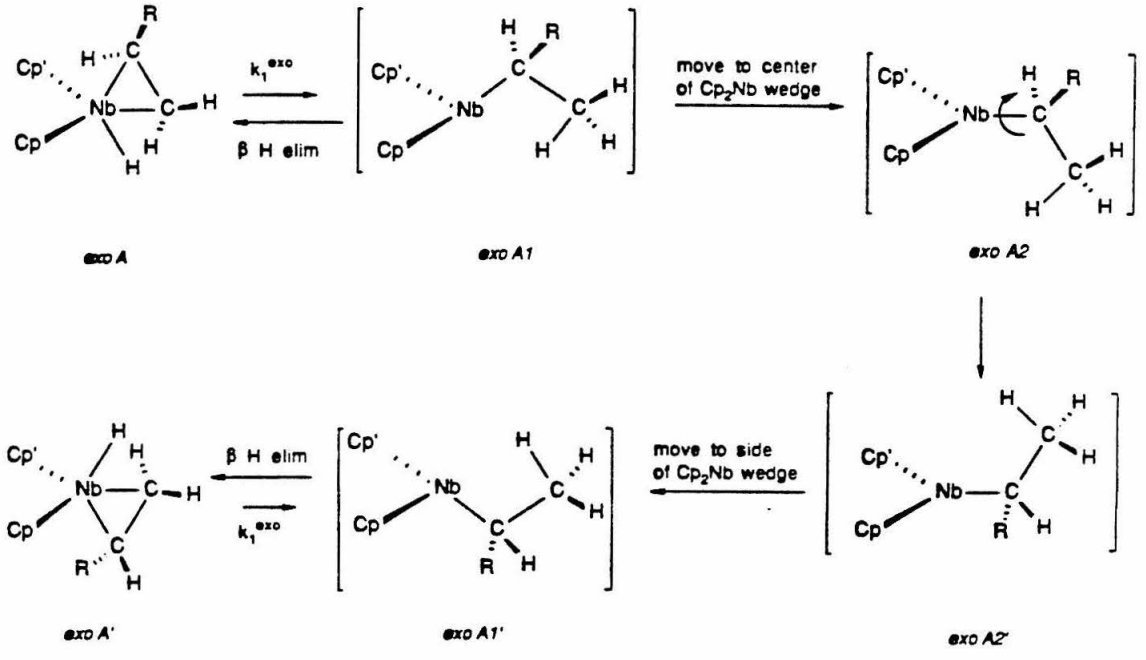


Table IV. Insertion rates for niobium and tantalum propene hydride complexes.[a]

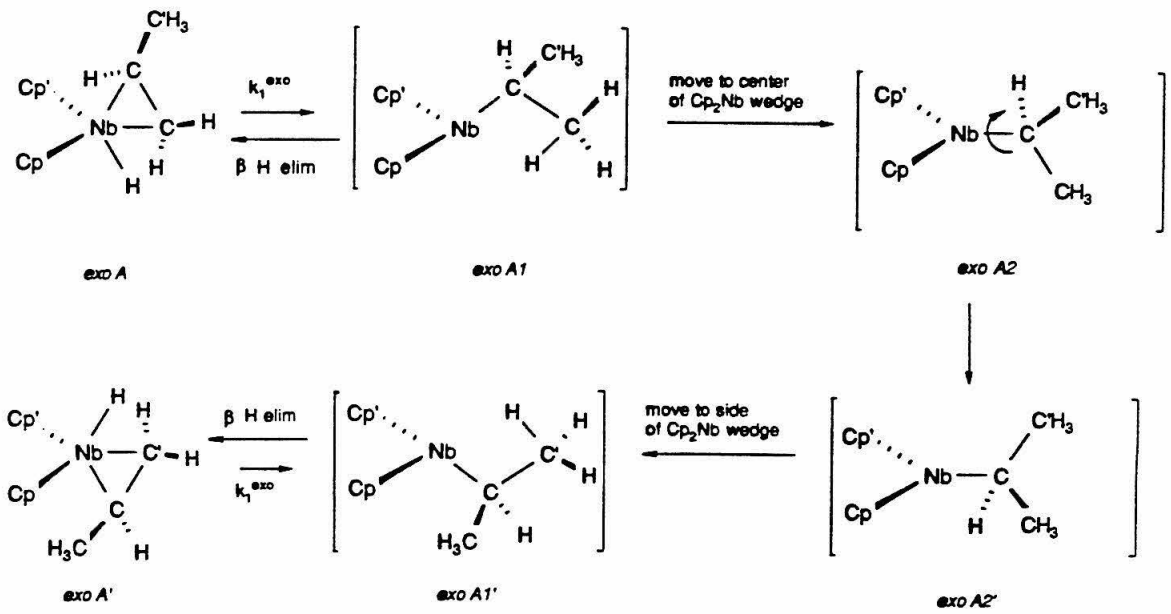
Compound		T(°C)	$k_1(s^{-1})$	$\Delta G^{\ddagger}(T)^b$
endo-$Cp^*_2Nb(CH_2=CHCH_3)H$	(*endo*-**10**)[c]	-1(1)	25.3(11)	14.1(1)
endo-$Cp_2Nb(CH_2=CHCH_3)H$	(*endo*-**11**)	45(5)	30.0(10)	16.5(3)
exo-$Cp_2Nb(CH_2=CHCH_3)H$	(*exo*-**11**)[d]	75(5)	7.0(10)	19.1(3)
	(*exo*-**11**)[e]	37(1)	2.1(1)	17.7(1)
endo-$Cp^*_2Ta(CH_2=CHCH_3)H$	(*endo*-**12**)	72(1)	26.0(10)	18.1(1)
endo-$Cp_2Ta(CH_2=CHCH_3)H$	(*endo*-**13**)	101(1)	28.2(10)	19.6(1)
exo-$Cp_2Ta(CH_2=CHCH_3)H$	(*exo*-**13**)[d]	139(1)	7.1(10)	22.8(1)

[a] Obtained by Cp ring coalescence at 90 MHz unless otherwise noted. [b] Reported in kcal·mol^{-1}. [c] Data taken from reference 2b. [d] Lower limits for k_1 and upper limits for $\Delta G^{\ddagger}(T)$. See text for explanation. [e] Measured by magnetization transfer from $CH_3CH=CH_2$ to $[CH_3CH=CH_2 + TaH]$.

We were unable to use coalescence methods to determine the insertion rate constants for the other olefin hydride complexes. The proton NMR signals of the Cp rings of the *endo*- and *exo*-isomers of the styrene complexes overlap, making it difficult to determine coalescence. Moreover, the niobocene complexes have much lower thermal stability than the analogous permethylniobocene, tantalocene or permethyltantalocene derivatives, partially decomposing before the coalescence temperature (>100°C) can be attained. An additional complication arises in the case of the *exo* isomers: the rate of exchange of the two cyclopentadienyl ring sites is slower than olefin insertion into the Nb-H bond. As shown in Scheme 2, after *exo A* undergoes olefin insertion the alkyl group of *A1* must "swing" to the center of the equatorial plane of the bent sandwich structure (*A1* ⟶ *A2*), undergo rotation about the Nb-$CHRCH_3$ bond (*A2* ⟶ *A2'*), "swing" to the other side of the wedge (*A2'* ⟶ *A1'*), and β-H eliminate in order to exchange Cp sites (*exo A* ⟶ *exo A'*). Inspection of the results for *exo*-**2** reveals that the barrier of 17 kcal·mol^{-1} for exchange of Nb-*H* with $PhCH=CH_2$ by magnetization transfer (*vide infra*) is considerably less than the ≈19 kcal·mol^{-1} barrier for Cp site exchange (see Table V). Thus, there appears to be a non-negligible barrier for passing the Nb(-$CHRCH_3$) group through the center of the wedge and/or rotating about the Nb-C_α bond.

A further complication arises in the calculation of k_1^{exo} by magnetization transfer for the *exo* propene hydride complexes. Since the methyl groups of the isopropyl ligand, generated by insertion from the *exo* propene hydride, may be related by a mirror plane (*exo A2* and *exo A2'*, Scheme 3) magnetization is exchanged between the Nb-*H*, Nb(CH_2=CHCH_3), *and* Nb(CH_2=CHCH_3) signals. We can treat this as a two-site exchange system[14] by monitoring the magnetization transfer between [Nb-*H* + Nb(CH_2=CHCH_3)] and Nb(CH_2=CHCH_3). As shown in Scheme 3, this still requires the "swinging" process but not a complete rotation (a methyl group does not have to be a full 90° out of the plane of the wedge) to lead to exchange. Qualitatively we see transfer between the Nb-*H* and the Nb(CH_2=CHCH_3) at about the same rate as the exchange into the other methyl group, and this rate is found to be much faster than that for Cp exchange.[15] The insertion rates and barriers for *exo*-Cp_2Nb(H)(CH_2=CHCH_3) and *exo*-Cp_2Ta(H)(CH_2=CHCH_3) are listed together with the data for the *endo* isomers in Table V, but, for the reasons stated above, they represent lower limits for k_1^{exo} and upper limits for $\Delta G^{\ddagger}$. The rate constants for Cp site exchange for the *endo* propene hydride derivatives (like the *endo* styrene hydride derivatives) are, however, simply ½ k_1^{endo}.

Scheme 3



The rates of olefin insertion (k_1) for both isomers of the niobocene styrene hydride complexes (**2-5**) were successfully determined by magnetization transfer experiments (^{1}H NMR, 500 MHz), and the results are summarized in Table V. Applications of this method to the closely related $Cp^*_2Nb(CH_2{=}CHR)H$ systems have been described previously.[2] By measuring the direct exchange between $Cp_2Nb(CH_2{=}C\mathit{H}R)H$ and $Cp_2Nb(CH_2{=}CHR)\mathit{H}$, this technique circumvents many of the difficulties present in the coalescence experiments. Moreover, this method allowed the determination of the rate constants at much lower temperatures (25-100°C) than the coalescence procedure and thus lessened the problem of sample decomposition. A difference NOE experiment performed for $Cp_2Nb(CH_2{=}CHC_6H_5)H$ at -10°C (where magnetization transfer is slow) verified that the NOE enhancement between the exchanging sites was negligibly small. The various vinylic and hydride signals were selectively irradiated, and no detectable NOE was found to occur between the hydride and the vinylic protons, although there was some enhancement observed between the various vinylic signals. These results suggest that the magnetization transfer data are not complicated by competing exchange and NOE effects.

Table V. Rates of olefin insertion for *exo*- and *endo*-$Cp_2Nb(CH_2{=}CHC_6H_4$-*p*-X)H complexes.[a]

Compound	X	T(°C)	$k_1(s^{-1})$	$\Delta G^{\ddagger}(T)$[b]	$k_1(s^{-1})^{50°C}$	$\Delta G^{\ddagger}(50°)$[b]
endo-**2**	H	89(1)	5.6(2)	20.1(1)	0.09(2)	20.5(1)
endo-**3**	CF_3	101(1)	3.2(2)	21.2(1)	0.01(1)	21.7(1)
endo-**4**	OMe	84(1)	5.3(3)	19.8(1)	0.15(2)	20.2(1)
endo-**5**	NMe_2	83(1)	6.6(4)	19.6(1)	0.21(3)	20.0(1)
exo-**2**[c]	H	25(1)	2.2(5)	17.0(2)		
exo-**2**	H	26(1)	2.2(3)	17.0(1)		
exo-**2**	H	36(1)	5.9(3)	17.0(1)	30(1)	16.8(1)
exo-**2**	H	46(1)	21.1(20)	16.8(1)		
exo-**2**	H	52(2)	36.7(15)	16.8(1)		
exo-**3**	CF_3	28(1)	5.8(5)	16.6(1)	58(6)	16.3(1)
exo-**3**[d]	CF_3	57(1)	0.50(5)	19.4(1)		
exo-**4**	OMe	36(1)	4.2(3)	17.2(1)	18(2)	17.1(1)
exo-**5**	NMe_2	37(1)	3.2(2)	17.5(1)	8.5(10)	17.6(1)

[a] All rate constants measured by magnetization transfer on a Bruker WM-500 in C_6D_6 unless otherwise noted. [b] Reported in kcal · mol^{-1}. [c] Measured in DMF-d_7. [d] Rate of Cp exchange measured by magnetization transfer.

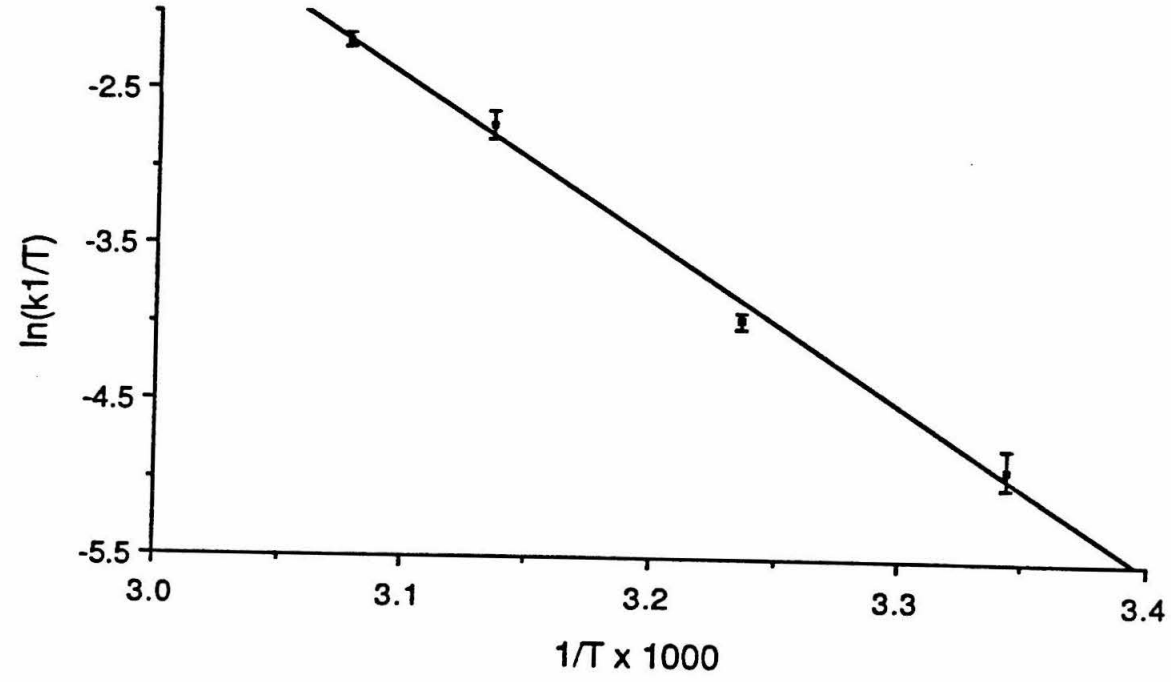


Figure 3. Eyring plot for olefin insertion of *exo*-$Cp_2Nb(H_2C{=}CHC_6H_5)H$: $\Delta H^{\ddagger}$ = 20.7 kcal · mol^{-1}, $\Delta S^{\ddagger}$ = +12 e.u., and R = 0.997.

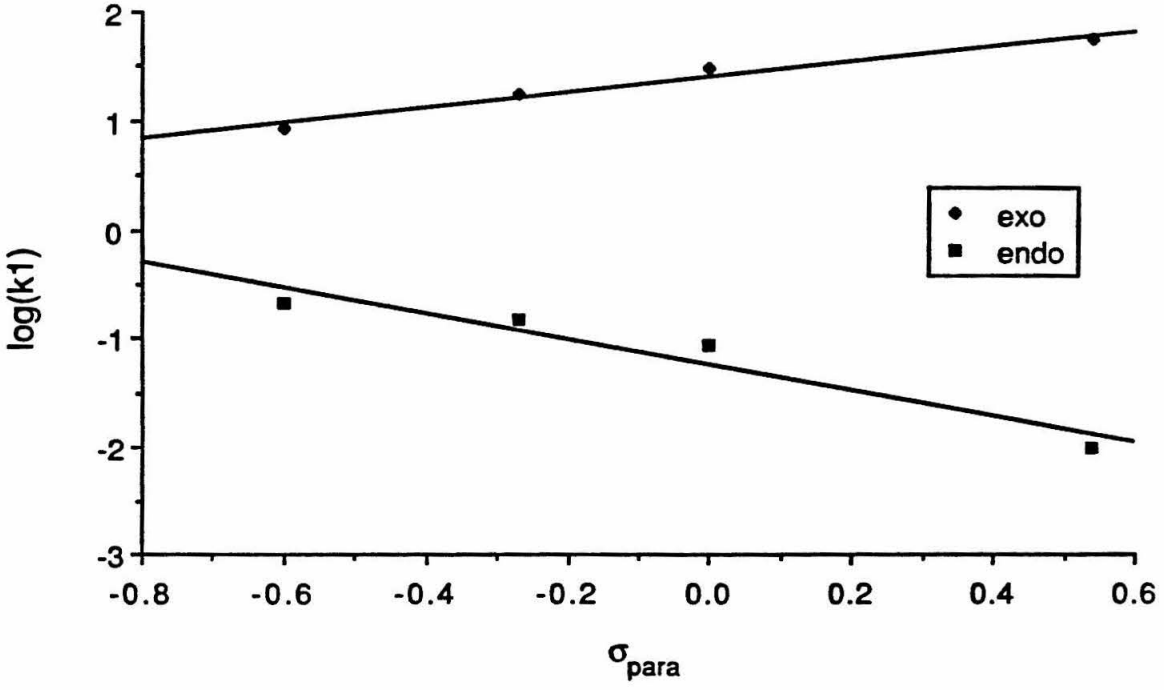


Figure 4. Hammett plots for olefin insertion in *exo*- and *endo*-$Cp_2Nb(H_2C{=}CHC_6H_4$-*p*-X)H *vs.* σ_p (errors are roughly the size of the points): ρ(*exo*) = 0.72, R = 0.986; ρ(*endo*) = -1.06, R = 0.966.

The activation parameters for the insertion reaction of *exo*-$Cp_2Nb(CH_2{=}CHC_6H_5)H$ were determined over the temperature range 27-52°C. An Eyring treatment of these data (Figure 3) yields $\Delta H^{\ddagger}$ = 20.7(7) kcal · mol^{-1}, $\Delta S^{\ddagger}$ = +12(2) e.u., with $\Delta G^{\ddagger}$(50°C) = 16.8(1) kcal · mol^{-1}. As was found for the permethylniobocene compounds ($\Delta S^{\ddagger}$ = +7 ± 5 e.u.)[2,12], the $\Delta S^{\ddagger}$ value is fairly small.[16] The *exo* styrene hydride isomers are found to have much lower barriers to insertion (consistently 3-5 kcal · mol^{-1} less) than the corresponding *endo* isomers. Hammett plots of the rate data (normalized to 50°C for comparison) for the *para*-substituted styrene-hydride derivatives show reasonable correlations with σ_{para} for both isomers (Figure 4), although the correlation for the *endo* derivatives is noticeably curved. The *endo* isomers exhibit faster rate constants with electron releasing substituents (ρ = -1.1, R = 0.966), while for the *exo* derivatives the rate increases systematically as the electron withdrawing power of the substituent increases (ρ = 0.7, R = 0.986).

By combining the equilibrium olefin binding data, which orders the ground states, with the kinetic data, the relative energies of the transition states ($\Delta G°_{TS} = \Delta G°_{GS} + \Delta G^{\ddagger}$) can be derived (Scheme 4). Again, the *exo* levels show a good correlation with σ_p with a ρ value of +2.8 (R = 0.996), however the *endo* levels correlate quite well with σ_+ (ρ_+ = 0.55, R = 0.994)[17]; thus explaining why the *endo* rate data do not correlate particularly well with either σ_{para} or σ_+ (the ground states correlate with σ_{para} and the transition states with σ_+).

The insertion rate of the permethylniobocene styrene hydride was measured in several solvents in the initial study and no determinable solvent effect was observed.[2b] A magnetization transfer measurement in DMF-d_7 (the most polar solvent compatible with these compounds) was performed for *exo*-$Cp_2Nb(CH_2{=}CHC_6H_5)H$. At 25°C the insertion rate in this solvent (Table V) was found to be identical, within experimental error, to that measured in benzene. Although a complete analysis has not been performed, these results suggest that there can be only a very small solvent effect on the olefin insertion process for these systems.

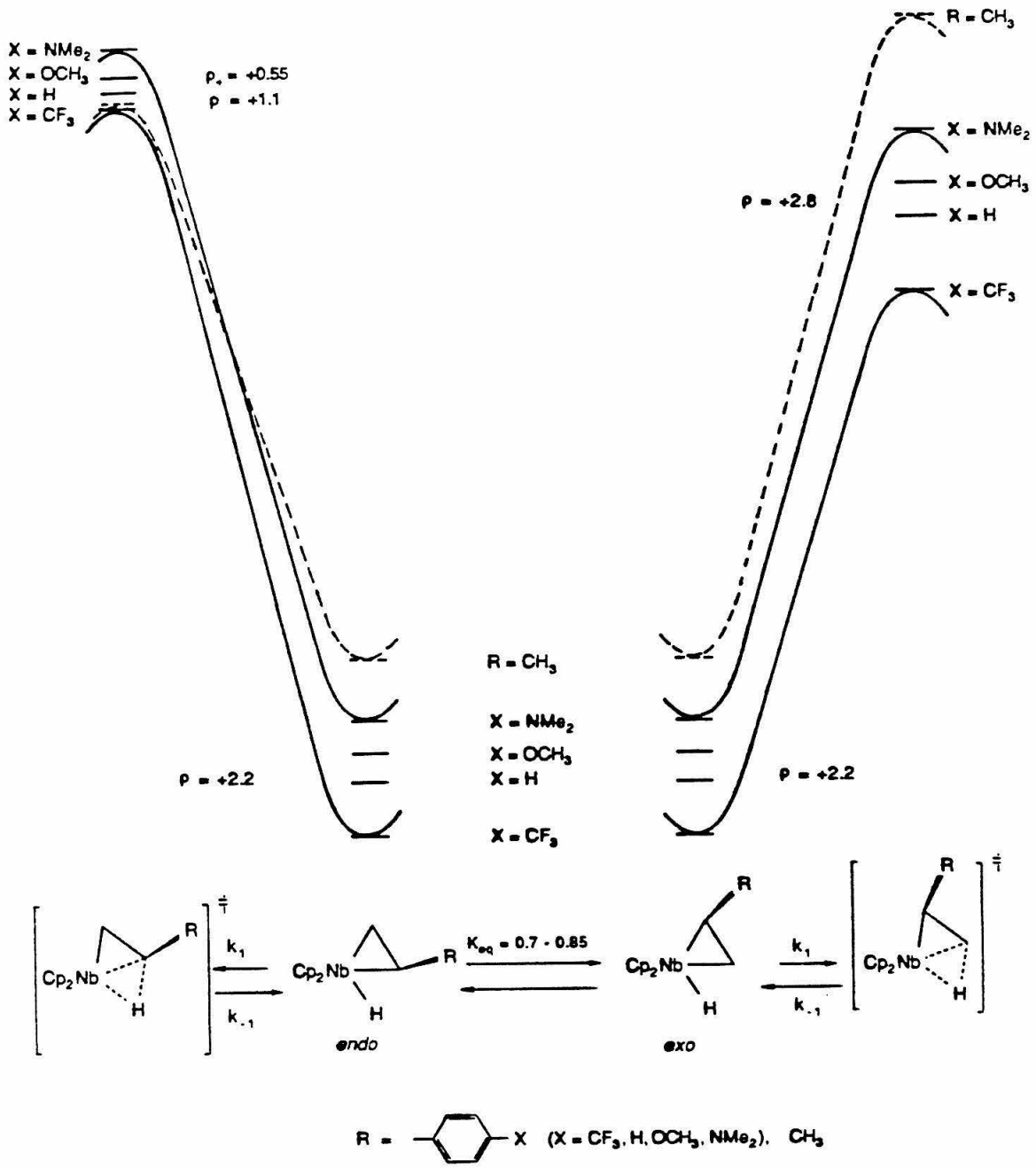
The results of the magnetization transfer experiments for the ethylene hydride derivatives **6-9**, are given in Table VI. The tantalum complexes undergo insertion more slowly than the niobium complexes, whereas the (η^5-C_5H_5) derivatives insert more readily than do the (η^5-C_5Me_5) analogs. As might be expected, the ethylene complexes exhibit a rate intermediate between the extremes set by the *endo* and *exo* styrene hydride derivatives.

Table VI. Olefin insertion rates for niobium and tantalum ethylene hydride complexes.

Compound		T(°C)	$k_1(s^{-1})$	$\Delta G^{\ddagger}(T)^a$
$Cp_2Nb(CH_2{=}CH_2)H$	(6)	33(1)	2.8(3)	17.3(1)
		45(1)	9.3(3)	17.2(1)
$Cp^*_2Nb(CH_2{=}CH_2)H$[b]	(7)	50(1)	2.6(2)	18.3(1)
$Cp_2Ta(CH_2{=}CH_2)H$	(8)	74(1)	1.0(1)	20.4(1)
$Cp^*_2Ta(CH_2{=}CH_2)H$	(9)	100(1)	2.4(1)	21.3(1)

[a] Reported in kcal·mol^{-1}. [b] Data taken from reference 2b.

Scheme 4

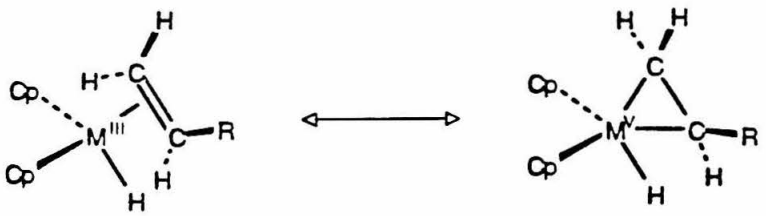

X = NMe2
X = OCH3
X = H
X = CF3
ρ+ = +0.55
ρ = +1.1
ρ = +2.2
R = CH3
X = NMe2
X = OCH3
X = H
X = CF3
ρ = +2.8
ρ = +2.2
Cp2Nb
H
R
k1
k-1
endo
Keq = 0.7 - 0.85
exo
R = X (X = CF3, H, OCH3, NMe2), CH3

DISCUSSION

Relative Rates of Insertion for Permethylmetallocene and Metallocene Ethylene and Propene Hydride Complexes of Niobium and Tantalum: Sterics *vs.* Electronics. Comparison of the rate constants (k_1) for insertion among the four ethylene hydride complexes $(C_5R_5)_2M(H)(H_2C{=}CH_2)$ (R = H, CH_3; M = Nb, Ta) highlights the magnitude of electronic effects within this family of compounds (Tables VI and VII). A smooth progression for k_1 is observed: $[Cp_2Nb] > [Cp^*_2Nb] > [Cp_2Ta] > [Cp^*_2Ta]$. This trend is readily accommodated by considering the insertion reaction simply as a reductive process: the formally M(V) metallacyclopropane hydride (Figure 5) being converted to the M(III) alkyl intermediate. NMR and structural data for these compounds indicate substantial metallacyclopropane (*vis-a-vis* M(III) olefin adduct) character in the ground state. Hence, the faster rates for the (η^5-C_5H_5) complexes as compared with the corresponding (η^5-C_5Me_5) complexes is attributable to increased stabilization of the ground state by the better donor ability of the latter. Similarly, replacement of Nb (4d metal) by Ta (5d metal) stabilizes M(V) relative to the M(III), again favoring the ground state relative to the transition state, according to the Hammond principle.[5]

Table VII. Relative olefin insertion rates for *endo*-[M]($H_2C{=}CHR$)H complexes at 50 °C.

[M] =	Cp_2Nb	Cp^*_2Nb	Cp_2Ta	Cp^*_2Ta
R = H	540	100	4	1
R = CH_3	115	4800	1	10



(a) (b)

Figure 5. Limiting forms of the metal olefin bonding interaction: (a) metal olefin adduct. (b) metallacyclopropane.

The importance of steric destabilization of the ground state relative to the transition state is readily appreciated by comparing the results for the family of *endo*-propene complexes (Tables IV and VII). Again the tantalum compounds have considerably larger barriers than their niobium analogs due to increased stability of Ta(V) *vs.* Ta(III) relative to Nb(V) *vs.* Nb(III). Significantly, the order reverses from that seen for the ethylene complexes when the Cp *vs.* Cp* comparison is made; the more electron releasing pentamethylcyclopentadienyl compounds show lower barriers to insertion by about 1-2 kcal·mol^{-1}. Larger steric interactions for the ground state *vs.* alkyl tautomer (and thus the transition state[5]) must be responsible for this reversal. Although the methyl group is expected to be bent back away from the metal in the ground state, the propyl tautomer (and hence transition state) is clearly less sterically congested, so that sterics are expected to accelerate insertion for the permethylmetallocene derivatives. The much lower binding constant for propylene relative to ethylene[2] in the permethylniobocene system is also likely to be largely a consequence of these unfavorable steric interactions between the methyl group and a (η^5-C_5Me_5) ligand. Although the electronic effects operating in the ethylene system are almost certainly acting here also, the steric effects of the bulky Cp* rings appear to override them for the propene hydride series. The magnitude of these effects suggests that it should be possible to modify the selectivity of systems of this type by playing off electronic and steric interactions.

Kinetic and Thermodynamic Analysis of the Niobocene Styrene Hydride System. A previous work attempted to detail the electronic effects that are operating in the styrene hydride insertion mechanism for the permethylniobocene system. It was found, however, that sterics moderated the electronic effects, and the linear free energy correlation indicated a ρ of only -0.64.[2b] The results described above for the ethylene and propylene complexes help to document the relative importance of steric and electronic effects at the transition metal center, but the effects originating from the olefin are not readily apparent. The *para* substituted styrene hydride complexes of *bis*(cyclopentadienyl)niobium provide an almost ideal system in which to study electronic effects associated with the olefin. Since both *exo* and *endo* isomers are

obtained in nearly equal proportions, steric interactions must be of much less consequence, and electronic effects are expected to be prominent.

The relative ground state energies of the various niobocene styrene hydride complexes have been measured by competitive equilibrium binding and are summarized in Table III. Whereas the ground state energies for the permethylniobocene styrene compounds are essentially invariant to *meta*- or *para* substitution, the niobocene system shows a strong dependence on the *para* substituent giving a very linear plot of log K_{eq} *vs.* σ_{para} with a substantial ρ value of +2.2. The positive value of ρ is as anticipated, since more π-acidic olefins (those with electron-withdrawing substituents) are expected to form more stable adducts. The *exo* to *endo* isomer ratio is almost invariant to substitution, indicating little steric or electronic preference for α- or β-substitution. The magnitude of these effects suggests that the phenyl ring is likely in resonance with the Nb-olefin bond for the less crowded (η^5-C_5H_5) complexes.

The olefin insertion kinetics for the *endo*-$Cp_2Nb(H)(CH_2{=}CHC_6H_4$-*p*-X) were measured by magnetization transfer techniques and are summarized in Table V. Qualitatively these results are similar to those found in the analogous permethylniobocene system: electron releasing substituents increase the insertion rate. The rate data show a rough correlation[18] with σ_{para} with a ρ value of -1.1, approximately double that found for the [Cp^*_2Nb] system. Without the rigid steric demands, the electronic effects seem more able to exert themselves. On closer analysis some important differences become evident, however. Considering both the competitive binding and rate data, the transition state orderings can be obtained, giving the energy diagram shown in Scheme 4. The relative orderings of the transition state energies for the *endo* derivatives are reversed from those that might be expected by comparing only the relative insertion rates and from those found for the permethylniobocene system.[2] This curious feature likely arises from a competition between ground state and transition state effects. Since the transition state appears to be essentially nonpolar, the stabilization of the positive charge buildup on the β-carbon would be expected to be relatively minor and thus unable to overcome

the other effects. A Hammett plot of the transition state data shows a linear correlation with σ_+, further suggesting that for the [Cp_2Nb] system the phenyl ring and the olefin π system can come into complete resonance in the transition state for the *endo* derivatives.

The insertion rates for the *exo*-$Cp_2Nb(H)(CH_2{=}CHC_6H_4$-*p*-X) complexes were also measured by magnetization transfer and are summarized in Table V. Interestingly, these compounds exhibit much lower insertion barriers than the corresponding *endo* isomers. Plots of log k_1 correlate with σ_{para} and give a ρ value of +0.7: electron-withdrawing substituents accelerate the insertion process. Plotting the transition state energy levels reveals that they are well separated and correlate with σ_{para} (ρ = +2.8). It appears that in this case, the ground state and transition state effects are working in concert and thus are additive (2.2 + 0.7 = 2.9, very close to the observed value of 2.8). The rather poor correlation with σ_+ in this case could indicate unfavorable steric interactions between the phenyl ring at C_α and a Cp ligand for [Cp_2Nb-$CH(C_6H_4X)(CH_3)$], although the rather small preference ($\leq$ 0.2 kcal $\cdot$ mol^{-1}) for the *endo* isomers suggests that steric interactions are *not* dominating the insertion process for the *exo* or *endo* complexes in the niobocene system.

These data indicate the following electronic effects are operating: (*i*) electron-withdrawing substituents at either C_α or C_β stabilize the ground state and increase the olefin binding constant, (*ii*) electron-releasing substituents at C_β accelerate the insertion process by stabilizing the modest positive charge build up at this position, (*iii*) electron-withdrawing substituents at C_α accelerate the insertion process. The origin of the third effect is not entirely clear. Consideration of the energy surface for the insertion reveals that there is a net increase in the Nb-C_α bonding with the transition state more closely resembling the [Cp_2Nb-$CH(C_6H_5)(CH_3)$] tautomer. Electron withdrawing groups should enhance the ionic character of the Nb-C bonding and increase the bond strength accordingly. Alternatively, there could be negative charge build up at C_α, which is stabilized by the electron-withdrawing substituents. The distinction between these two possibilities is not sharp; however, we tend to

favor the picture based on relative bond strengths. The magnitude of the kinetic ρ's (-1.1 for the *endo* and +0.7 for the *exo* isomers) indicates only a modest amount of charge development in the transition state. Moreover, the reaction rates for both the permethylniobocene and niobocene systems are not enhanced in polar solvents as would have been expected for a highly charged transition state.

In comparing the effects of alkyl and aryl groups on the rate constants and ground state orderings, the aryl group appears to generally be functioning as electron withdrawing (sp^2 hybridized C) relative to the methyl group (sp^3 hybridized C). If C_β did approach the limit of a tricoordinate carbocation in the transition state, one would expect the *endo* styrene hydride complex to undergo insertion much faster than the propene hydride complex, since the benzylic carbonium ion is much more stable than a secondary carbonium ion.[19] However, neither of these two limiting features is achieved in the transition state for olefin insertion for these group 5 metallocene systems: the magnitude of ρ indicates relatively little positive charge development, and the coordination number of C_β approaches four, not three ($C_\beta \longrightarrow$ sp^3 hybridization) in the transition state. Thus, the full extent of resonance stabilization of the carbonium ion normally afforded by the phenyl substituent is not available in the bridged ([Nb···H···C_β]) transition state, and inductive destabilization by the sp^2 phenyl further slows the rate of insertion for the styrene hydride complex. A similar reversal of effects for aryl *vs.* alkyl has been noted for electrophilic attack at olefin proceeding *via* bridged transition states[20].

The electronic effects observed for the $Cp_2Nb(CH_2{=}CHC_6H_4\text{-}p\text{-}X)H$ compounds are strikingly similar to those reported by Halpern and Okamoto for insertion of styrenes into Rh-H bonds[1g]. These authors found a smaller ground state substituent effect (ρ = +1.0) and a similar substituent effect on the rate of insertion (ρ = -0.9). Although the direction of insertion was not established for this system, the opposing electronic effects are as we find for the *endo*-$Cp_2Nb(CH_2{=}CHC_6H_4\text{-}p\text{-}X)H$ series of complexes, suggesting that $[L_2(H)RhCH_2CH_2C_6H_4X]$ rather than $[L_2(H)RhCH(CH_3)C_6H_4X]$ is the insertion product.

CONCLUSIONS

A comparison of the olefin insertion rates for the family of compounds $(C_5R_5)_2M(CH_2=CHR')H$ (R, R' = H, CH_3; M = Nb, Ta) indicates the major metal and ancillary ligand electronic and steric effects that are of importance in the olefin insertion reaction. Empirically it appears as if the reaction can be viewed as a reductive (M^V to M^{III}) process in the case of ethylene with no bulky substituents. The activation barriers to olefin insertion increase in the order Cp_2Nb < Cp^*_2Nb < Cp_2Ta < Cp^*_2Ta as would be expected. When substituents are present on the olefin, the electron donating ability of the cyclopentadienyl ring becomes much less important as steric interactions begin to dominate the course of the reaction.

The large electronic effects found in the $Cp_2Nb(CH_2=CHC_6H_4$-p-X)H system reinforce the steric arguments made to explain the relative indifference of the permethylniobocene complexes to substituents. The system with the much less bulky cyclopentadienyl rings shows a sizable dependence on the identity of the coordinated olefin and on the location of substituents. Steric interactions seem to be sufficiently small so as not to disrupt the resonance between the phenyl ring and the vinyl group, as evidenced by the strong dependence of the olefin binding constants on the nature of the olefin. This also leads to significant effects in the transition states although these are not particularly straightforward to interpret. Essentially, electron-releasing substituents are favored at the β-carbon and electron-withdrawing substituents are favored at the α-carbon, however, these can be attenuated or enhanced by the strong ground state effect.

The results are all in accord with the four-centered transition state that has been previously postulated for these types of processes. Moreover, the small to modest linear free energy relationships and indifference to solvent effects suggest that, while a small amount of charge must build up, the transition state is fairly nonpolar and remains highly bonded. Thus olefin insertion appears to be a highly concerted process that is dependent upon a very delicate balance of steric and electronic effects.

EXPERIMENTAL SECTION

General Considerations. All air sensitive manipulations were carried out using glove box or high vacuum line techniques. Solvents were dried over CaH_2 or sodium benzophenone and stored over titanocene. Benzene-d_6 and toluene-d_8 were dried over activated 4 Å molecular sieves and stored over titanocene. 1,4-dioxane-d_8 was also dried over sieves but stored over sodium benzophenone. Dimethylforamide(DMF)-d_7 was dried and stored over activated alumina. Argon was purified by passage over MnO on vermiculite and activated molecular sieves.

NMR Spectra were recorded on Varian EM-390 (^{1}H, 90 MHz), JEOL FX90Q (^{1}H, 89.56 MHz), JEOL GX400Q (^{1}H, 399.78 MHz; ^{13}C, 100.38 MHz) and Bruker WM500 (^{1}H, 500.13 MHz) spectrometers. Infrared spectra were recorded on a Beckman 4240 spectrometer and peak positions are reported in cm^{-1}. All elemental analyses were conducted by L. Henling of the Caltech Analytical Laboratory.

Starting Materials. Styrene (Aldrich), *para*-methoxystyrene (Aldrich), and ethyl magnesium chloride and *n*-propyl magnesium bromide in diethyl ether solution (Aldrich) were used without further purification. *para*-Trifluoromethylstyrene and *para*-dimethylaminostyrene were prepared as described previously.[2b]

$Cp_2Nb(CH_2{=}CHCH_3)H$[6c] **(11)**, and $Cp_2Ta(CH_2{=}CHCH_3)H$[6b] **(13)** were prepared by literature methods. $Cp_2Nb(CH_2{=}CH_2)H$ **(6)** and $Cp_2Ta(CH_2{=}CH_2)H$ **(8)** were prepared by the method previously reported for Ta[6d] except that the reactions were carried out under argon rather than ethylene to prevent formation of the $Cp_2M(CH_2{=}CH_2)(CH_2CH_3)$ complexes. Cp_2NbCl_2 and Cp_2TaCl_2 were prepared using the trialkyltin reagent as reported by Green[21] and purified by Soxhlet extraction into methylene chloride. The published procedure was followed for the synthesis of Cp_2NbH_3[22] **(1)** from Cp_2NbCl_2 and $LiAlH_4$, the product being purified by sublimation (60-70°C, 10^{-3} torr). The syntheses of $Cp^*_2Ta(CH_2{=}CHCH_3)H$ **(12)** and

$Cp^*_2Ta(CH_2{=}CH_2)H$ (**9**) from $Cp^*_2TaCl_2$ and the appropriate Grignard reagent (*n*-propyl and ethyl, respectively) have recently been developed in our laboratory.[7]

$Cp_2Nb(CH_2{=}CHC_6H_5)H$ (2). Styrene (1 mL, 9 mmol) was syringed into a toluene solution of **1**, Cp_2NbH_3, (0.782 mg, 3.5 mmol) against an argon counterflow at room temperature. After stirring overnight (12-24 hr) at 25°C, the resulting orange-yellow solution was filtered and 994 mg (88%) of yellow microcrystalline **2** (≈ 1:1 mixture of *endo* and *exo* isomers) isolated by slow precipitation with petroleum ether. IR (Nujol): 3111, 3093, 3072, 3032, 1727, 1589, 1566, 1489, 1433, 1365, 1298, 1287, 1222, 1176, 1149, 1118, 1075, 1069, 1016, 1008, 898, 841, 822, 800, 782, 754, 727, 698, 538. Mass Spectrum (m/e): 328(M^+), 224, 223, 104. Anal. Calcd. for $C_{18}H_{18}Nb$: C, 65.86; H, 5.83. Found: C, 65.28; H, 5.85.

$Cp_2Nb(CH_2{=}CHC_6H_4$-*p*-$CF_3)H$ (3). The above procedure (for **2**) was followed using **1** (0.8 g, 3.54 mmol) and 1.5 mL (9 mmol) of *p*-trifluoromethylstyrene. Precipitation yielded 850 mg (61%) of yellow-green microcrystalline **3**. IR (Nujol): 1720, 1601, 1508, 1320, 1219, 1180, 1148, 1103, 1060, 1005, 839, 809, 779, 714. Mass Spectrum (m/e): 396(M^+), 243, 242, 224, 223, 172, 159. Anal. Calcd. for $C_{19}H_{18}F_3Nb$: C, 57.59; H,4.58. Found: C,56.99; H, 4.55.

$Cp_2Nb(CH_2{=}CHC_6H_4$-*p*-OMe)H (4). The above procedure (for **2**) was followed with **1** (124 mg, 0.55 mmol) and 0.25 mL (1.9 mmol) of *p*-methoxystyrene. Precipitation yielded 146 mg (74%) of yellow-green microcrystalline **4**. IR (nujol): 3085, 3068, 3018, 1740, 1713, 1695, 1600, 1567, 1502, 1440, 1299, 1289, 1242, 1229, 1160, 1148, 1140, 1101, 1060, 1032, 1016, 1009, 836, 793, 779, 720. Mass Spectrum (m/e): 358(M^+), 224, 223, 134. Anal. Calcd. for $C_{19}H_{21}ONb$: C, 63.70; H, 5.91. Found: C, 63.28; H, 5.81.

$Cp_2Nb(CH_2{=}CHC_6H_4$-*p*-$NMe_2)H$ (5). The above procedure (for **2**) was followed with **1** (0.740 g, 3.27 mmol) and 1.3 mL (8.5 mmol) of *p*-dimethylaminostyrene. Precipitation yielded 1.1 g (91%) of yellow-microcrystalline **5**. IR (Nujol): 3077, 3029, 1717, 1610, 1552, 1512, 1341, 1299, 1234, 1218, 1190, 1163, 1148, 1111, 1058, 1013, 1006, 945, 849, 838, 807, 780, 720. Mass

Spectrum (m/e): 371(M^+), 224, 223, 147. Anal. Calcd. for $C_{20}H_{24}NNb$: C, 64.69; H, 6.52; N, 3.77. Found: C, 64.50; H, 6.54; N, 3.82.

$Cp_2Nb(C{\equiv}NMe)(NMe_2)$. Methylisocyanide (300 torr in ≈400 mL at 298K, 6.5 mmol) was condensed into a solution of **1** (512 mg, 2.27 mmol) in 30 mL of petroleum ether at -78°C. This mixture was allowed to warm to 25°C and stirred for 48 hours resulting in a maroon solution. This solution was filtered, concentrated to about 20 mL, and slowly cooled to -78°C to afford 592 mg (84% yield) of the pure product as violet needles. IR (Nujol): 3100, 2789, 2715, 1879(m), 1782(vs), 1414, 1260, 1218, 1164, 1108, 1014, 996, 955(s), 943, 794(s). Mass Spectrum (m/e): 308(M^+), 267, 224, 223. Anal. Calcd. for $C_{14}H_{19}N_2Nb$: C, 54.56; H, 6.21; N, 9.09. Found: C, 54.54; H, 6.09; N, 9.02.

Competitive Binding Measurements. Samples of niobocene styrene complex (**2**) with excess propene or one of the substituted styrenes or samples of compounds **3-5, 9** with excess styrene were prepared in benzene-d_6 and sealed under argon in an NMR tube. These were allowed to reach equilibrium at 25°C, and the equilibrium constants were determined by measuring the amounts of each species by ^1H NMR (500 MHz). Errors were determined by estimation of the integration errors and by comparing the values obtained by approaching the equilibrium from different sides.

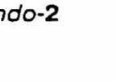
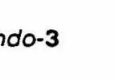
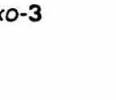
Difference NOE Experiments. All difference NOE experiments were carried out on the WM-500 spectrometer. In the experiment to assign the isomers, each of the four Cp resonances was selectively irradiated and the resulting spectrum subtracted from the standard spectrum, allowing the complete correlation of the various vinylic and hydride signals with the proper Cp signal. A second experiment was performed at -10°C in toluene-d_8 in which each of the eight hydride and vinylic resonances was selectively irradiated in order to determine the extent of the NOE enhancement between the exchanging sites. The results showed no observable NOE enhancement between the exchanging hydride and vinylic signals although some was observed between the cyclopentadienyl and vinylic signals.

Measurement of Olefin Insertion Rates Using Coalescence Techniques. Coalescence temperatures of the two C_5R_5 resonances for the olefin hydride complexes **11-13** were measured at 90 MHz on a JEOL FX90Q spectrometer. A typical sample was prepared in a glove box by loading the olefin hydride complex (≈20 mg) and benzene-d_6 (0.4 mL) in a sealable NMR tube. Tubes were sealed either at -196°C under an atmosphere of nitrogen or at -78°C under 700 torr argon. The temperature at which coalescence occurs was measured by the peak separation of an ethylene glycol sample. The room temperature ^{1}H NMR spectrum was recorded before and after determination of the coalescence temperature; no decomposition was evident. The rate of exchange at the coalescence temperature was calculated using the Gutowsky-Holm approximation, $k_{exchange}(T_c) = (\pi/\sqrt{2})\Delta\nu$,[23] where $\Delta\nu$ is the frequency separation between the C_5R_5 peaks in the room temperature spectrum. The rate of insertion in these cases is related to the exchange rate by a factor of two: $k_1(T_c) = 2k_{exchange}(T_c) = \sqrt{2}\pi\Delta\nu$. $\Delta G^{\ddagger}(T_c)$ can be calculated from the Eyring Equation, $\Delta G(T_c) = RT_c\ln(\kappa kT_c/k_c h)$,[24] assuming a transmission coefficient, κ, of 1.

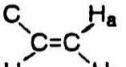
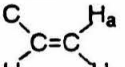
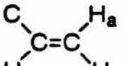
Measurement of Olefin Insertion Rates Using Magnetization Transfer Techniques. All magnetization transfer experiments were performed on a Bruker WM-500 spectrometer. Samples were prepared as described above for the coalescence experiments. The sample temperature was maintained by the WM-500 variable temperature unit and were determined to be constant to within ±1°C by measuring the temperature before and after the experiment with an ethylene glycol sample. For some of the higher temperature experiments (≥80°C) the appearance of the sample and the NMR spectrum indicated a small amount of decomposition (≤3%) but this did not appear to affect the results. The relaxation times (T_1) were measured at each temperature by an inversion recovery pulse sequence and analyzed by a three-parameter fitting routine. Magnetization transfer experiments were performed by selectively inverting one of the exchanging signals with a single decoupler pulse and then waiting a variable delay time (τ) before executing the observation pulse. Measurements were generally made for 15-20 τ values spanning a range from milliseconds to several times the T_1 values. The spectrometer's

automatic integration routine was used to obtain lists of the peak areas. Peak intensities were determined as ratios of the areas of the exchanging resonances to a constant resonance. A four parameter nonlinear least-squares fit of the differences of the inverted resonance and the exchanging resonance as a function of delay time to the magnetization equation was performed using a version of the computer program written by Perkin[25]. Errors in k_1 were propagated from the standard deviation calculated for $k_{exchange}$ by the curve-fitting routine.

TABLE 1. ^{1}H and ^{13}C NMR Data for niobocene olefin hydride complexes.

Compound	Assignment		δ/ppm (Coupling/Hz) ^{1}H	δ/ppm (Coupling/Hz) ^{13}C
$Cp_2Nb(CH_2{=}CHC_6H_5)H$[a]	C_5H_5		4.48(s)	94.2(d,quin; 175,7)
	C_5H_5		4.35(s)	93.5(d,quin; 175,7)
	Nb-*H*		-2.41(s,br)	
endo-**2**		H_a	1.28(dd; 13.0, 5.5)	
		H_b	0.92(dd; 10.1, 5.5)	
		H_x	3.32(dd; 10.1, 13.0)	
	$=CH_2$			13.9(dd; 148,149)
	=*C*HPh			33.9(d; 143)
	C_6H_5		6.8-7.6[b]	153.6(s)
				127.9(dd; 156,7)
				126.6(d,br; 155)
				122.1(dt; 158,7)
$Cp_2Nb(CH_2{=}CHC_6H_5)H$[a]	C_5H_5		4.52(s)	93.5(d,quin; 175,7)
	C_5H_5		4.25(s)	92.7(d,quin; 175,7)
	Nb-*H*		-2.89(s,br)	
exo-**2**		H_a	1.62(ddd; 13.1, 6.9, 1.7)	
		H_b	1.45(ddd; 10.0, 6.9, 2.2)	
		H_x	2.58(dd; 10.0, 13.1)	
	$=CH_2$			9.1(td; 151,5)
	=*C*HPh			35.3(d 142)
	C_6H_5		6.8-7.6[b]	152.8(s)
				127.5(dd; 155,7)
				126.6(d,br; 155)
				121.6(dt; 157,7)
$Cp_2Nb(CH_2{=}CHC_6H_4\text{-}p\text{-}CF_3)H$[a,c]	C_5H_5		4.42(s)	94.6(d,quin; 175,7)
	C_5H_5		4.25(s)	94.0(d,quin; 176,7)
	Nb-*H*		-2.47(s,br)	
endo-**3**		H_a	1.11(dd; 13.1, 5.8)	
		H_b	0.85(dd; 9.8, 5.8)	
		H_x	3.08(dd; 9.8, 13.1)	
	$=CH_2$			14.1(dd; 146,147)
	=*C*HPh			33.6(d; 148)
	C_6H_5		6.8-7.6[b]	159.2(s)
				120-130[b]
$Cp_2Nb(CH_2{=}CHC_6H_4\text{-}p\text{-}CF_3)H$[a,c]	C_5H_5		4.45(s)	93.7(d,quin; 176,7)
	C_5H_5		4.13(s)	93.1(d,quin; 175,7)
	Nb-*H*		-2.82(s,br)	
exo-**3**		H_a	1.44(ddd; 13.0, 9.9, 1.6)	
		H_b	1.37(ddd; 9.9, 6.9, 2.1)	
		H_x	2.36(dd; 9.9, 13.0)	
	$=CH_2$			9.7(dd; 145,146)
	=*C*HPh			34.3(d; 147)
	C_6H_5		6.8-7.6[b]	158.3(s)
				120-130[b]

Compound	Assignment		δ/ppm (Coupling/Hz) ^{1}H	δ/ppm (Coupling/Hz) ^{13}C
$Cp_2Nb(CH_2{=}CHC_6H_4\text{-}p\text{-}OMe)H$[a]	C_5H_5		4.48(s)	94.1(d,quin; 176,7)
	C_5H_5		4.37(s)	93.4(d,quin; 176,7)
	Nb-*H*		-2.47(s,br)	
endo-**4**		H_a	1.25(dd; 13.0, 5.4)	
		H_b	0.94(dd; 10.2, 5.4)	
		H_x	3.34(dd; 10.2, 13.0)	
	OCH_3		3.39(s)	55.04(q; 141)
	$=CH_2$			14.02(t; 150)
	=CHPh			33.38(d; 158)
	C_6H_5		6.8-7.6[b]	155.55(s),145.66(s)
				127.82(d; 155)
				113.42(dd; 157,4)
$Cp_2Nb(CH_2{=}CHC_6H_4\text{-}p\text{-}OMe)H$[a]	C_5H_5		4.52(s)	93.5(d,quin; 176,7)
	C_5H_5		4.28(s)	92.6(d,quin; 176,7)
	Nb-*H*		-2.94(s,br)	
exo-**4**		H_a	1.62(ddd; 13.1, 6.8, 1.8)	
		H_b	1.46(ddd; 10.1, 6.8, 2.3)	
		H_x	2.59(dd; 6.8)	
	OCH_3		3.41(s)	55.09(q; 141)
	$=CH_2$			8.77(t; 152)
	=CHPh			34.91(d; 149)
	C_6H_5		6.8-7.6[b]	156.01(s),145.66(s)
				127.82(d; 155)
				113.42(dd; 157,4)
$Cp_2Nb(CH_2{=}CHC_6H_4\text{-}p\text{-}NMe_2)H$[a]	C_5H_5		4.50(s)	93.8(d,quin; 175,7)
	C_5H_5		4.42(s)	93.1(d,quin; 175,7)
	Nb-*H*		-2.43(s,br)	
endo-**5**		H_a	1.36(dd; 13.0, 5.3)	
		H_b	0.99(dd; 10.3, 5.3)	
		H_x	3.44(dd; 10.3, 13.0)	
	$N(CH_3)_2$		2.61(s)	41.30(q; 134)
	$=CH_2$			14.39(t; 148)
	=CHPh			33.85(d; 149)
	C_6H_5		6.8-7.6[b]	146.62(s),141.70(s)
				127.44(d; 154)
				113.07(d; 154)

Compound	Assignment		δ/ppm (Coupling/Hz) ^{1}H	δ/ppm (Coupling/Hz) ^{13}C
$Cp_2Nb(CH_2{=}CHC_6H_4\text{-}p\text{-}NMe_2)H$[a]	C_5H_5		4.55(s)	93.3(d,quin; 175,7)
	C_5H_5		4.35(s)	92.3(d,quin; 175,7)
	Nb-*H*		-2.97(s,br)	
exo-**5**		H_a	1.73(ddd; 13.1, 6.6, 1.7)	
		H_b	1.52(ddd; 10.1, 6.6, 2.1)	
		H_x	—(dd; 10.1, 13.1)	
	$N(CH_3)_2$		2.63(s)	41.21(q; 134)
	$=CH_2$			9.02(t; 148)
	$=CHPh$			35.75(d; 147)
	C_6H_5		6.8-7.6[b]	147.01(s),140.78(s)
				127.44(d; 154)
				113.07(d; 154)
$Cp_2Nb(CH_2{=}CHCH_3)H$[d]	C_5H_5		4.58(s)	
	C_5H_5		4.44(s)	
	Nb-*H*		-2.95(s,br)	
endo-**10**		H_a	1.01(dd; 10.2, 4.1)	
		H_b	0.49(dd; 12.1, 4.1)	
		H_x	1.99(dd; 10.2, 12.1)	
	CH_3		1.93(d; 6.4)	
$Cp_2Nb(CH_2{=}CHCH_3)H$[d]	C_5H_5		4.47(s)	
	C_5H_5		4.44(s)	
	Nb-*H*		-3.19(s,br)	
exo-**10**		H_a	1.45(ddd; 10.1, 5.5, 1.9)	
		H_b	0.85(ddd; 12.3, 5.5, 1.4)	
		H_x	1.24(dd; 10.1, 12.3)	
	CH_3		1.64(d; 6.5)	
$Cp_2Nb(C{=}NCH_3)(N(CH_3)_2)$[e]	C_5H_5		5.08(s)	
	$C{=}NCH_3$		2.92(s)	
	$N(CH_3)_2$		2.76(s,br)	
$Cp_2Ta(CH_2{=}CH_2)(CH_2CH_3)$[d]	C_5H_5		4.49(s)	
	$=CH_2$		1.11(t; 11.1)	
	$=CH_2$		0.60(t; 11.1)	
	CH_2CH_3		1.32(q; 7.4)	
	CH_2CH_3		1.61(t; 7.4)	

[a] ^{1}H spectrum measured on a Bruker WM-500 spectrometer (500.13 MHz) in C_6D_6. ^{13}C spectrum measured on a JEOL GX-400 spectrometer (100.25 MHz) in d_8-dioxane. [b] The phenyl region was not resolved. [c] The ^{13}C resonance of the CF_3 group was not found. [d] ^{1}H spectrum measured on a Bruker WM-500 spectrometer (500.13 MHz) in C_6D_6. The high resolution ^{1}H NMR spectrum has not been previously reported for this compound. [e] Measured on a JEOL-FX-90Q spectrometer (90 MHz ^{1}H).

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9. Although not previously reported, this compound was assigned by its similarity (^{1}H NMR, C_6D_6) to the trimethylphosphine complex: δ_{Cp} = 4.63 (d, 2 Hz); δ_{OMe} = 3.28 (d, 10.3 Hz); δ_H = -7.45 (d, 33.3 Hz).

10. In this case a mixture of the ethylene hydride and ethylene ethyl complexes was obtained. See references 6a and 8a.

11. Such a species has been observed in the permethylniobocene system: Doherty, N. M. Ph.D. Thesis, California Institute of Technology, 1984.

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13. The value of k_1 is, in fact, equal to $2k_{exchange}$ (at all temperatures), since, on average, two k_1 events are required to effect ring site exchange; see Johnson, C. S. Jr. *Adv. Magn. Reson.* **1965**, *1*, 33-102 (in particular pp. 64-82) and references therein for discussion of relevant examples. This factor of two was not used in the previously reported experiments with *endo*-$Cp^*_2Nb(CH_2{=}CHR)H$ (ref. 2). While the conclusions from the previous works are unchanged, using the correct values of k_1 (for the points derived from coalescence experiments) in the Arrhenius plots (Figure 4 and Table IV of reference 2b; Figure 4 of the Supplementary Material of ref 2c) leads to a better correlation and slight change in $\Delta S^{\ddagger}$ from -7 (±5) e.u. to +7 (±5) e.u., with the corresponding small changes in $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$.

14. The quantitative analysis of multiple site magnetization transfer, while possible, is not straightforward. We have not attempted such a treatment. See, for example: Muhandiram, D. R.; McClung, R. E. D. *J. Magn. Reson.* **1987**, *71*, 187-92.

15. This observation seems to indicate that rotation is the slow step of Cp ring exchange for these *exo* complexes rather than "swinging" through the center of the wedge, however this latter process may still contribute slightly to the overall exchange rate.

16. In normalizing rate constants to a standard temperature (50°C for comparison[2]), the assumption has been made that $\Delta S^{\ddagger} = +7$ (±5) e.u. for all compounds[13].

17. To the extent that the phenyl ring is in direct resonance with the incipient β carbon (but not the α carbon) in the transition state, σ_+ should correlate better than σ_p for the *endo*-styrene-hydride complexes, and σ_p should correlate better than σ_+ for the *exo*-styrene-hydride complexes. This is, in fact, the case.

18. The line obtained is fairly curved, however. Apparently differing degrees of resonance stabilization are operating for the ground and transition states; the ground states correlate best with σ_p whereas the transition states correlate best with σ_+.

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CHAPTER 2

Synthesis, Characterization, and Reactivity of Permethyltantalocene Benzyne and Phenyl Complexes.

Abstract: Coordinatively unsaturated [$Cp^*_2Ta\text{-}C_6H_5$], generated by reduction/metathesis of $Cp^*_2TaCl_2$ with LiC_6H_5 in toluene, rapidly undergoes a β-hydride elimination reaction to yield a novel benzyne hydride complex. Dynamic NMR experiments indicate that this complex exists in an equilibrium with the unobserved sixteen electron phenyl tautomer and allow the determination of the rate of hydride migration (k_1). The primary mode of reactivity for this

$$Cp^*_2Ta(\eta^2\text{-}C_6H_4)H \underset{}{\overset{k_1}{\rightleftharpoons}} [Cp^*_2Ta\text{-}C_6H_5] \xrightarrow{L} Cp^*_2Ta(C_6H_5)L$$

system is *via* the phenyl and not the benzyne tautomer, thus reactions with a wide variety of ligands, L, afford trapped $Cp^*_2Ta(C_6H_5)L$ complexes (L = CO, RCN, O_2, O, CH_2, *etc.*). This family of compounds exhibits some interesting properties and chemistry which will be discussed. For instance, model compounds for the study of reductive-elimination, α-migratory insertion, nitrile activation, and oxidation chemistry have been obtained. Reaction with XH-type substrates (XH = HO-H, RO-H, RCOO-H, *etc.*) often leads to loss of benzene and formation of [Cp^*_2TaX] complexes, presumably also *via* the phenyl tautomer.

INTRODUCTION

Our group has recently been interested in the chemistry of permethyltantalocene complexes which we have found to be very amenable for study due to their high thermal stability.[1] In particular, the [Cp^*_2Ta] fragment has been found to form an entire family of complexes in which there is a dynamic equilibrium between a more stable Ta(V) species and an unobserved Ta(III) species:

$$[Cp^*_2Ta\text{-}XZ] \rightleftharpoons Cp^*_2Ta(=X)Z \qquad [X\text{-}Z = CH_2\text{-}H,\ CH{=}CH\text{-}H]$$

$$[Cp^*_2Ta\text{-}XYZ] \rightleftharpoons Cp^*_2Ta(\eta^2\text{-}XY)Z \qquad [XY\text{-}Z = CH_2CH_2\text{-}H,\ OCH_2\text{-}H,\ MeNCH_2\text{-}H]$$

As was shown in the previous chapter, permethyltantalocene olefin complexes possess high barriers to β-migratory insertion due to stabilization of the Ta(V) ground state *vs.* the Ta(III) alkyl intermediate. In retrospect, this may be an unsurprising result since the third row metals prefer higher oxidation states and the electron-rich [Cp^*_2Ta] unit undergoes strong backbonding with unsaturated organic fragments. Thus, the right side of the above equilibria are generally favored, although the coordinatively unsaturated tautomers are accessible and often much more reactive.

Transition metal benzyne complexes have been elusive intermediates that have been proposed to play roles in such diverse processes as decomposition reactions of metal polyaryls,[2] dinitrogen functionalization,[3] and C-H bond activation.[4] Since the first isolated mononuclear benzyne complex was reported by Schrock in 1979,[5] there has been increased interest in the chemistry of these types of species. Transition metal benzyne intermediates have been invoked in many reaction schemes but have been most studied in the thermolysis reactions of Group IV $(C_5R_5)_2MAr_2$ complexes.[6] While the structures and reaction chemistry have been briefly explored for the few stable examples,[7] very little is known about their mechanisms of formation or reactivity except from indirect evidence. As a notable exception,

Buchwald has recently been exploring the utility of both isolable and transient zirconocene benzyne moieties in organic synthesis.[8]

If the benzyne ligand is considered to resemble the coordinated olefins that were examined in the previous chapter, it might be expected that the permethyltantalocene fragment would be a good choice for stabilizing such complexes. Indeed, we have recently been able to generate [Cp^*_2Ta-C_6H_5] which rapidly undergoes a β-hydrogen elimination reaction to form a novel benzyne hydride complex. The reactive phenyl intermediate can also be trapped by a wide variety of ligands and thus provides a synthetic precursor for $Cp^*_2Ta(L)Ph$ model compounds. The syntheses and chemistry of these tantalum benzyne and phenyl complexes are described herein.

RESULTS AND DISCUSSION

Synthesis and characterization of permethyltantalocene benzyne complexes. Treatment of $Cp^*_2TaCl_2$ with at least two equivalents of phenyl lithium in toluene affords the η^2-benzyne hydride complex (**1**). Removal of the biphenyl by-product by sublimation and workup with pentane gives **1** as a tan solid in approximately 50-75% yield. Presumably the first equivalent of phenyl lithium acts as a reducing agent to afford a tantalum (III) mono-chloride species which is metathesized by the second equivalent to give [Cp^*_2Ta-C_6H_5] (Eq. 1). These types of reactions are well known in niobocene and tantalocene chemistry.[9] The coordinatively unsaturated phenyl complex then undergoes a rapid β-H elimination to afford the eighteen electron tantalum (V) benzyne hydride.

$$Cp^*_2TaCl_2 \xrightarrow[\text{-LiCl, Ph-Ph}]{\text{LiPh}} [Cp^*_2TaCl] \xrightarrow[\text{-LiCl}]{\text{LiPh}} [Cp^*_2Ta\text{-}C_6H_5] \xrightarrow{\beta\text{-H}} \underset{\mathbf{1}}{Cp^*_2Ta(\eta^2\text{-}C_6H_4)H} \quad (1)$$

The room temperature ^1H NMR spectrum (Table I) is as expected, showing a single Cp* resonance at δ 1.61 and the Ta-H as a broad singlet at δ 2.24. The four aromatic hydrogens

appear as two broad lumps at low field (90 MHz) but at higher field show the expected pattern (Figure 1-a). As with all these benzyne and phenyl complexes, NMR spectra in d_8-dioxane (*vs.* d_6-benzene) exhibit more well separated aryl hydrogen and carbon signals, leading to easier assignment. The ^{13}C NMR spectrum shows the benzyne carbons (C_1 and C_2) as broad singlets at δ 158.9 and 157.2. These chemical shifts are considerably further upfield than those observed by Schrock for his tantalum benzyne complex[5] and are in the range exhibited by normal aryl carbons bonded to tantalum (*vide infra*). This trend may be a reflection of the higher electron-donating ability of the [Cp^*_2Ta] fragment. Complete ^1H and ^{13}C NMR data are summarized in Tables I and II. The infrared, analytical, and mass spectral data are summarized in the experimental section and are in accord with the benzyne hydride formulation.

Attempts to extend this methodology for the preparation of complexes of substituted benzynes have proved less successful. Under the above conditions, *m*-tolyllithium and *p*-tolyllithum, but not *o*-tolyllithium, give the desired benzyne products, but aryl lithiums with other substituents (OMe, NMe_2, and CF_3) give either paramagnetic oils or mixtures of products. One of the products observed in the Li-C_6H_4-*m*-OMe reaction might indicate a reaction with the Cp* ligand. Due to the dual nature of these alkyl lithium reduction/metathesis reactions, it appears that they are quite sensitive to a variety of factors that affect the relative rates of reduction and metathesis (the nature of the metal center, the alkyl group, the solvent, *etc.*). It has also been observed that reductions of $Cp^*_2TaCl_2$ with active metals in THF in efforts to prepare [Cp^*_2TaCl] instead appear to yield $Cp^*_2Ta(H)Cl$ as the final product.[10]

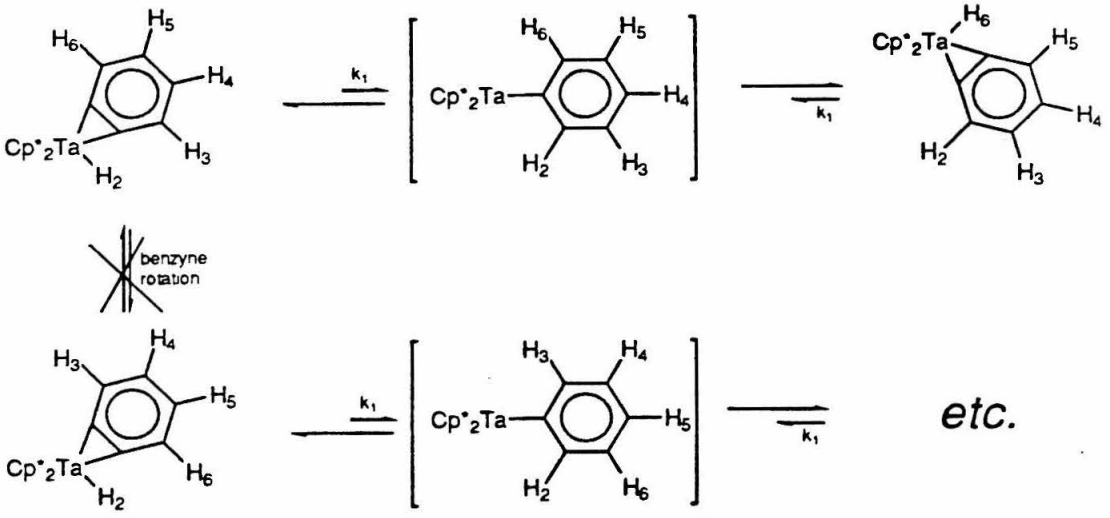
Extension to other tantalocene systems has also proven to be quite limited. Neither Cp_2TaCl_2 or $Cp^*CpTaCl_2$ has been found to react with phenyllithium under a variety of conditions to form a benzyne hydride species. It seems that in these less sterically encumbered cases that the [$(C_5R_5)_2TaCl$] compound formed by reduction can react with itself or the starting dichloride to form an insoluble, unreactive material. For example, a reaction of Cp_2NbCl and Cp_2NbCl_2 to form a dimeric product has previously been reported.[11] Success

has been achieved, however, for a substituted tantalocene, $Cp^*Cp^{\phi}TaCl_2$ ($Cp^{\phi} = \eta^5$–C_5Me_4Ph), that has previously demonstrated a close resemblance to the [Cp^*_2Ta] system.[1c]

It was also of interest to prepare $Cp^*_2Ta(\eta^2\text{-}C_6H_4)X$ complexes primarily in hopes of studying the insertion reactions into metal alkyl as well as metal hydride bonds. As an extension of the known chemistry of other metal hydride complexes, the most obvious procedure for functionalizing **1** was *via* treatment with MeI to yield methane and $Cp^*_2Ta(\eta^2\text{-}C_6H_4)I$ (**5**). This reaction does indeed provide **5** as a product, but there also appears to be a paramagnetic side product. Aside from such preparative difficulties, the iodide complex also does not appear to react readily with alkylating reagents. Thus the chemistry of this interesting class of compounds has not yet been fully explored.

Study of the *β*(*ortho*)-hydrogen insertion/elimination reaction. Dynamic NMR experiments indicate that **1** exists in a rapid equilibrium with the phenyl tautomer (Scheme 1). Since exchange is only observed for $H_2 \lhd\!\!\rightarrow H_6$ and $H_3 \lhd\!\!\rightarrow H_5$ to over 100°C (Figure 1), benzyne rotation must be slow on the NMR time scale. For instance, if rotation were to occur as shown in the bottom of Scheme 1, H_4 would also be expected to exchange with the other aryl hydrogens and thus not remain the sharp triplet as observed in the variable temperature NMR experiment. The hindered rotation is likely due to steric interactions with the bulky pentamethylcyclopentadienyl ligands and to the fact that the out-of-plane orbitals are of higher energy than those in the wedge[12] and likely do not lead to strong bonding in the perpendicular rotamer. The observed exchange can be explained by a simple rotation about the Ta-Ph bond in the phenyl tautomer or by a process in which the phenyl group "swings" through the center of the wedge. While our results cannot distinguish between these two possibilities, high rotational barriers are observed for $Cp^*_2Ta(L)Ph$ complexes (*vide infra*) and for other [Cp^*_2Ta-R] bonds[13] causing us to favor the swinging process. The fact that solutions of the $Cp^*_2Ta(\eta^2\text{-}C_6H_3\text{-}4\text{-}Me)H$ and $Cp^*_2Ta(\eta^2\text{-}C_6H_3\text{-}3/5\text{-}Me)H$ complexes do not interconvert after months at room temperature indicates that benzyne rotation is slow even on the chemical time scale.

SCHEME 1



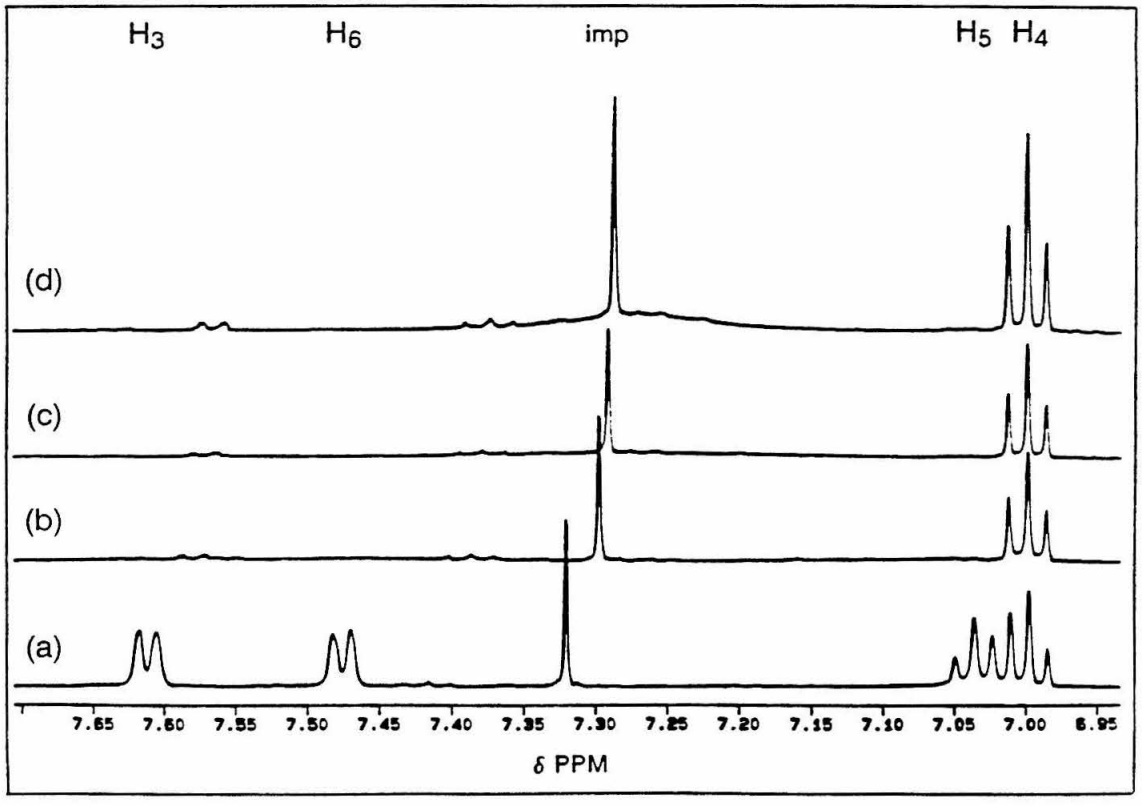


Figure 1. Variable temperature ^1H NMR spectrum (500 MHz; d_8-dioxane) of the aryl region of $Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$: (a) standard room temperature (25°C) spectrum. (b) 77°C. (c) 92°C. (d) at 102°C near coalescence of H_5 and H_3 (H_6 is coalescing with a peak more upfield).

By examining the exchange of $H_2 \lhd\!\!\rightarrow H_6$ or $H_3 \lhd\!\!\rightarrow H_5$ by coalescence or magnetization transfer techniques (see Chapter 1 for a discussion of these techniques), the benzyne insertion rate, k_1, can be measured over a remarkably wide range of temperatures (83°C). The results of these experiments are summarized in Table III. An Eyring treatment of these data (Figure 2) yields the activation parameters: $\Delta H^{\ddagger}$ = 14.4(3) kcal·mol^{-1}, $\Delta S^{\ddagger}$ = -7(1) e.u., and $\Delta G^{\ddagger}$(50°C) = 16.6(1) kcal·mol^{-1}. The small entropy of activation is in accord with a unimolecular reaction in which the transition state resembles the ground state. The 4-methyl substituted benzyne complex exhibits an only slightly faster rate of insertion (Table IV) indicating little substituent effect (although the effect of a methyl group is not expected to be very large).

These rates can be compared to the β-migratory insertion rates of the coordinated olefins measured in the previous chapter. It is apparent that the benzyne moiety more readily undergoes the insertion. This is likely due to a combination of reinforcing effects acting on both the benzyne hydride and the phenyl tautomers. For instance, there is almost certainly some strain in the benzyne (or *o*-phenylene) metal interaction, thus raising the relative energy of the ground state. Concurrently in these early transition metal systems, aryl groups are generally expected to form much stronger bonds to metals that normal alkyls. This effect should stabilize the [Cp*$_2$Ta-Ph] tautomer and, according to the Hammond postulate, consequently the transition state for benzyne insertion.

In order to help provide further mechanistic insight into other systems potentially involving benzynes, it was of interest to determine the kinetic isotope effect for substitution by deuterium. Although this requires a different technique for determining the kinetics, it can be accomplished by examination of the chiral mixed ring Cp*Cp$^{\phi}$Ta(η^2-C_6H_4)H and Cp*Cp$^{\phi}$Ta(η^2-C_6D_4)D complexes. Benzyne insertion to form the achiral phenyl intermediate leads to exchange of the two sets of diastereotopic methyl groups ($Me^a \lhd\!\!\rightarrow Me^d$, $Me^b \lhd\!\!\rightarrow Me^c$) on the Cp$^{\phi}$ ligand (Scheme 2). This exchange rate could be monitored by magnetization

Table III: Variable temperature kinetic data for benzyne insertion in $Cp^*_2Ta(\eta^2\text{–}C_6H_4)H$, 1.

T (K)	k_1 (s^{-1})	Method	$\ln(k_1/T)$
296(1)[a]	4.1(2)	MT 2 ⟶ 6	-4.279(50)
	4.2(3)	MT 6 ⟶ 2	-4.255(70)
306(1)[b]	10.8(4)	MT 2 ⟶ 6	-3.344(60)
	11.6(4)	MT 6 ⟶ 2	-3.273(60)
309(1)[a]	13.9(6)	MT 2 ⟶ 6	-3.101(50)
	12(1)	MT 6 ⟶ 2	-3.248(80)
319(1)[a]	30(2)	MT 2 ⟶ 6	-2.364(70)
349(3)[c]	178(10)	Coal 3 ⟷ 5	-0.673(60)
379(5)[d]	1304(100)	Coal 3 ⟷ 5	1.236(90)

a) Measured by magnetization transfer (MT) on a Bruker AM-500 NMR spectrometer in C_6D_6. b) Same as (a) but measured in d_8-dioxane. c) Measured by coalescence on a Jeol FX-90Q NMR spectrometer in d_8-dioxane. d) Measured by coalescence on a Bruker AM-500 NMR spectrometer in C_6D_6.

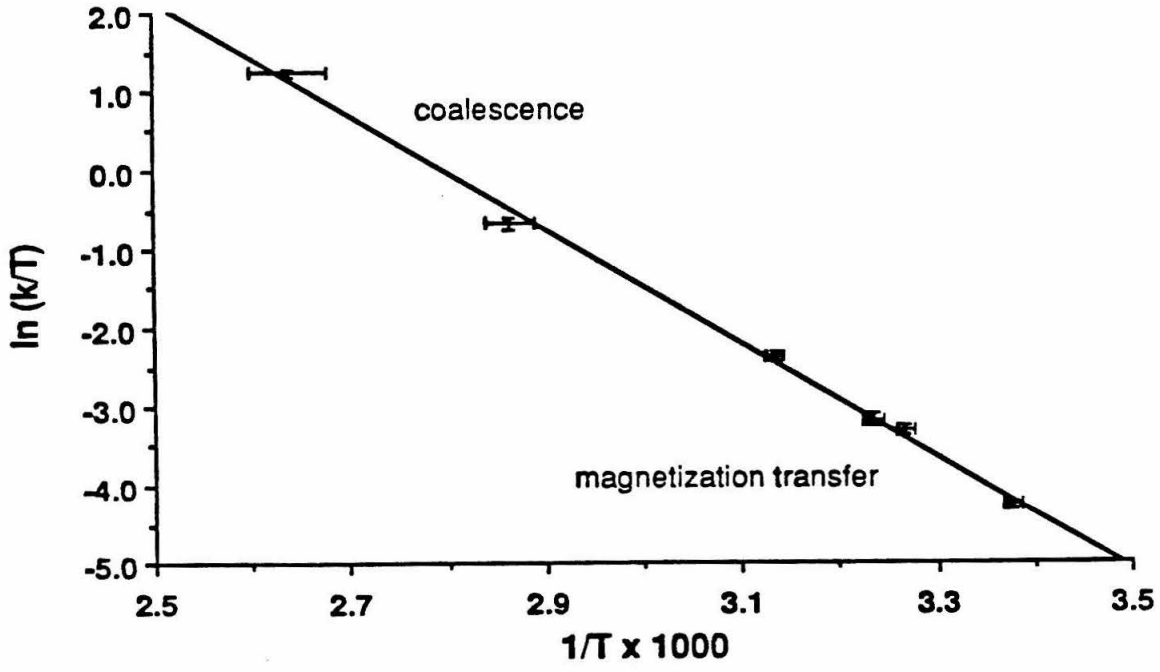


Figure 2. Eyring plot for the permethyltantalocene benzyne hydride (**1**) insertion reaction (k_1, Scheme 1): $\Delta H^{\ddagger}$ = 14.4(3) kcal · mol^{-1}, $\Delta S^{\ddagger}$ = -7(1) e.u., and $\Delta G^{\ddagger}$(50 °C) = 16.6(1) kcal · mol^{-1}.

transfer experiments and directly related back to the insertion rate. Such experiments (Table IV) indicated an isotope effect (k_H/k_D) of 2.5(3) at 32°C.

The deuterium isotope effects for comparable processes vary over a fairly wide range but do show a "normal" effect ($k_H/k_D > 1$). Olefin insertion in the related permethylniobocene system was shown to exhibit a k_H/k_D of 1.1 (4) at 105°C.[14] Isotope effects have also been measured for β-hydrogen abstractions from metal aryls in a tantalum system (k_H/k_D = 4.1(8) at 118°C)[15] and a zirconium system (k_H/k_D = 13.5(20) at 25°C; k_H/k_D = 6.5(10) at 70°C).[6d] Data have also been reported for the thermolysis of Cp_2TiPh_2 in the solid state from which isotope effects can be calculated (k_H/k_D = 1.5 at 70°C; k_H/k_D = 1.25 at 80°C; k_H/k_D = 1.06 at 90°C).[6b] The temperature dependence of these values makes it difficult to make detailed comparisons.

SCHEME 2

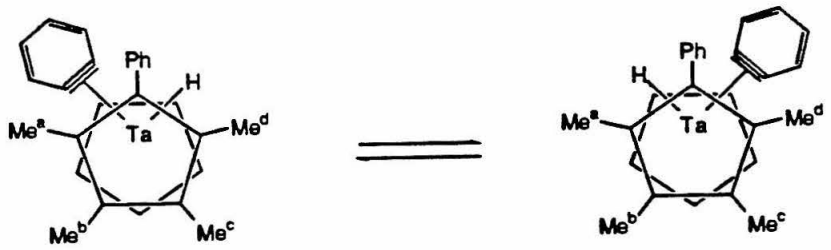


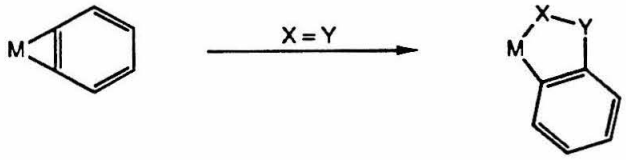
Table IV. Kinetic data for benzyne insertion reactions.[a]

Compound		Method	T (K)	k_1 (sec^{-1})	$\Delta G^{\ddagger}$ (T)[b]
$Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$	1	MT 2 ⇄ 6	306 (1)	11.2(4)	16.46
$Cp^*_2Ta(\eta^2\text{-}C_6H_3\text{-}(4\text{-}Me))H$	2	MT 3 ⇄ 5	306 (1)	12.2(6)	16.41
$Cp^*Cp^{\phi}Ta(\eta^2\text{-}C_6H_4)H$[c]	4	MT a ⇄ d	305 (1)	32.0 (20)	15.77
$Cp^*Cp^{\phi}Ta(\eta^2\text{-}C_6D_4)D$[c]	4-d_5	MT a ⇄ d	305 (1)	12.8(4)	16.32

(a) measured by magnetization transfer (MT) on a Bruker AM-500 NMR spectrometer in C_6D_6. (b) reported in kcal · mol^{-1}. (c) $Cp^{\phi} = \eta^5\text{-}C_5Me_4Ph$

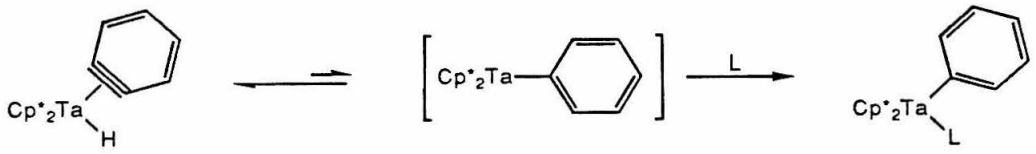
Reactivity of permethyltantalocene benzyne hydride complexes. Benzyne hydride complex **1** is quite stable under inert atmosphere conditions but reacts readily with oxygen or water (*vide infra*) in solution. The solid can be sublimed under high vacuum, with difficulty, at about 130°C although there is significant decomposition. Thermolysis of benzene solutions of **1** occurs only slowly at 120°C, resulting in metalation of the Cp* ligands to form benzene and the "tuckin" complexes: $Cp^*(\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2)_2)TaH$ and $(\eta^5,\eta^1\text{-}C_5Me_4CH_2)_2TaH_2$.[6e] Similar behavior is observed in the fragmentation pattern of the mass spectrum of **1**.

A common mode of reactivity for the previously known benzyne complexes has been the addition of unsaturated substrates to form metallaindan type products.[16]



The benzyne hydride system is quite different, however, since there is a facile migratory insertion pathway that makes the coordinatively unsaturated phenyl tautomer available. Indeed, the chemistry of these complexes is dominated by additions to this more reactive species, either of trapping ligands to form $Cp^*_2Ta(Ph)(L)$ type complexes or of HX type substrates to form products derived from $Cp^*_2Ta(H)(X)(Ph)$ moieties. The only case in which reactivity of the benzyne hydride tautomer has been observed is in the reaction with methyl iodide to form the benzyne iodide complex (*vide supra*). This transformation, however, exhibits low yields and paramagnetic side products possibly suggesting some type of competing electron transfer pathway with the phenyl tautomer.

Synthesis and characterization of simple $Cp^*_2Ta(L)(C_6H_5)$ adducts. As stated above, the benzyne hydride complex, **1**, reacts with a wide variety of donor ligands, L, to form the trapped phenyl complexes:



These adducts have been characterized by IR and NMR spectroscopy (see Tables I and II) and elemental analysis. Several characteristic features can be noted in the NMR spectra of these complexes. It appears that there is a rather high rotational barrier about the Ta-Ph bond (dynamic NMR experiments indicate a minimum rotational barrier of 21 kcal·mol^{-1} in $Cp^*_2Ta(=CH_2)Ph$), leading to 5 inequivalent hydrogen (see Figure 3) and 6 inequivalent carbon resonances. This property, presumably steric in origin, is quite common for these phenyl complexes and can have a dramatic effect on their chemistry (*vide infra*). A second common feature is that one of the *ortho*-H resonances tends to come relatively far downfield in d_6-benzene (δ 7.5-9.0). Difference NOE experiments performed for $Cp^*_2Ta(=CH_2)Ph$ indicate that it is the hydrogen that points toward the methylene ligand (H_2) that is the most downfield. It is assumed that this is the case for the other complexes as well. A brief compilation of the characteristic NMR parameters in d_6-benzene for several permethyltantalocene phenyl complexes can be found in Table V.

The simple CO and $CNCH_3$ adducts of permethyltantalocene phenyl are analogous to similar complexes that have been reported for other niobocenes and tantalocenes. The low IR stretching frequencies of the coordinated ligands (ν_{CO} = 1850 and ν_{CN} = 1759) indicate that the Cp^*_2Ta-Ph fragment is a good electron donor and participates in strong backbonding. These compounds, however, are quite thermally robust and appear to undergo no further chemistry. Several more interesting types of complexes are discussed below.

Table V. Characteristic ^1H NMR signals of permethyltantalocene phenyl complexes in C_6D_6.

Compound	δ Cp*	δ H_2	δ L
$Cp^*_2Ta(CS_2)Ph$	1.45	8.59	
$Cp^*_2Ta(CO_2)Ph$	1.48	8.31	
$Cp^*_2Ta(CO)Ph$	1.52	8.03	
$Cp^*_2Ta(O_2)Ph$	1.54	8.16	
$Cp^*_2Ta(N{\equiv}CSiMe_3)Ph$	1.58	≈7.98	
$Cp^*_2Ta(C{\equiv}NCH_3)Ph$	1.59	8.21	3.37
$Cp^*_2Ta(=CH_2)Ph$	1.69	7.60	10.14
$Cp^*_2Ta(H)_2Ph$	1.70	8.51	2.71, 0.95
$Cp^*_2Ta(=O)Ph$	1.71	7.89	
$Cp^*_2Ta(=N\text{-}CD{=}CD_2)Ph$	1.72	7.76	

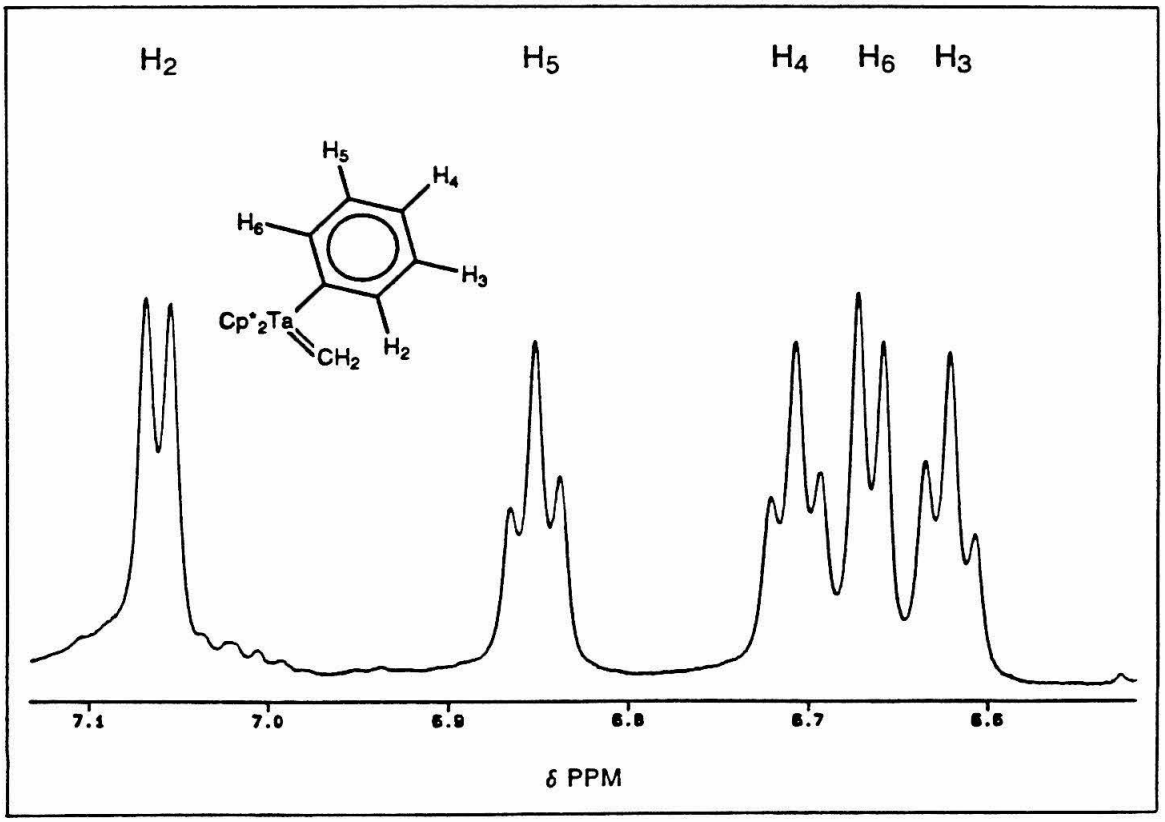
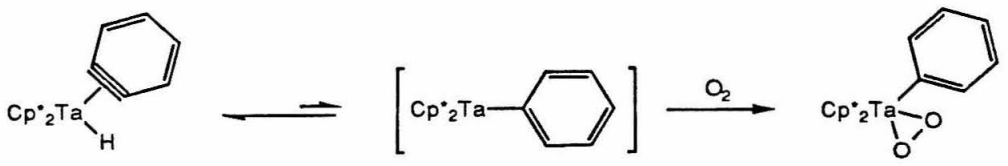


Figure 3. Phenyl region of the 500 MHz ^1H NMR spectrum of $Cp^*_2Ta(=CH_2)C_6H_5$ in d_8-dioxane demonstrating hindered rotation about the tantalum phenyl bond.

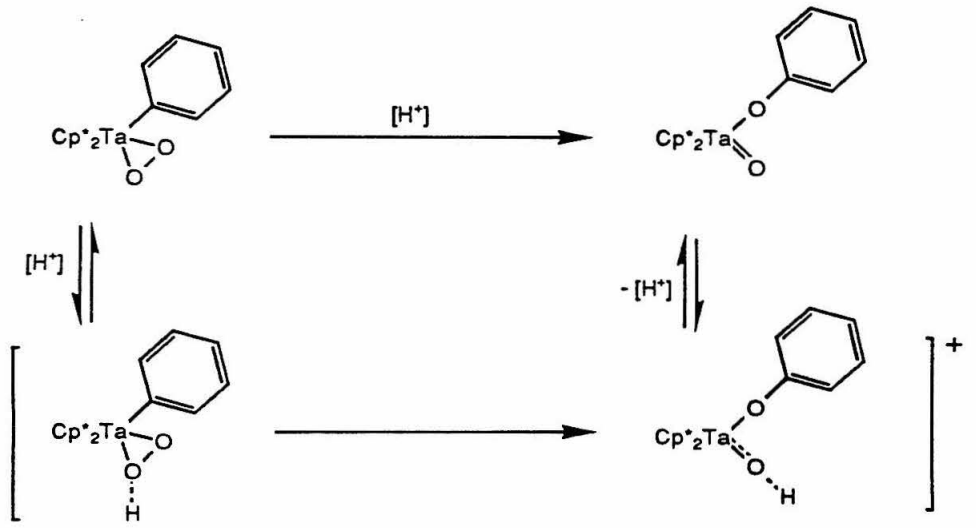
Oxygen transfer reactions. Under ambient conditions, **1** reacts cleanly with nitrous oxide to form $Cp^*_2Ta(=O)Ph$. Probably due to the highly oxophilic nature of the tantalum center, similar types of oxygen transfer chemistry are quite common for a wide variety of oxygen containing substrates (*e.g.*, epoxides and nitroalkanes).[17] **1** also reacts cleanly with O_2 to form an η^2-peroxo complex (Eq. 2), which can undergo a novel phenyl to oxygen migration, yielding



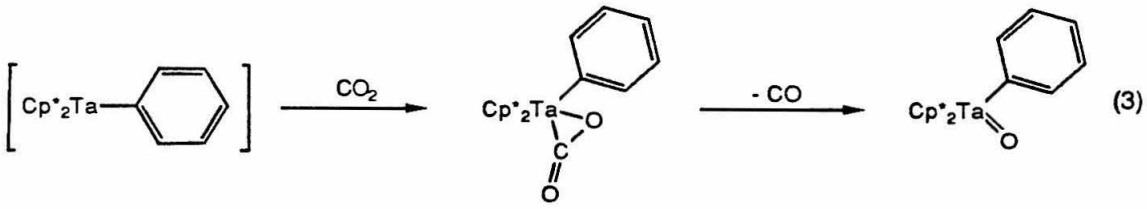
(2)

$Cp^*_2Ta(=O)OPh$. This transformation appears to be acid catalyzed and may proceed by a mechanism as outlined in Scheme 3.[18] It is hoped that the study of these types of processes will help to shed some light on the complicated but very important field of oxidation chemistry and work is proceeding to determine the detailed mechanism of these and related types of rearrangements. It is also of interest to determine if such complexes can serve to oxidize other organic substrates.

SCHEME 3



The reaction of **1** with carbon dioxide proceeds more slowly than with O_2 or N_2O and requires heating to 80°C to reach completion. The complex, **11**, thus formed is consistent with a simple CO_2 adduct resembling that reported for the niobocene system[19] rather than a metallacycle from reaction with the benzyne fragment as had been found for titanocene.[20] The ^{13}C NMR (δ CO_2 = 215.1) and infrared (ν_{CO} = 1699) parameters are in accord with this structure although an X-ray crystal structure determination would be needed to unambiguously characterize this compound.[21] Thermolysis of **11** at 100°C leads to a first order decomposition ($k^{100°C}$ = 9.2(1) x 10^{-6} s^{-1}; $\Delta G^{\ddagger}_{100°C}$ = 30.59(5) kcal·mol^{-1}) to $Cp^*_2Ta(=O)Ph$ (Eq. 3) with evolution of a noncondensible gas (0.8 equiv by Toepler) at liquid nitrogen temperature (77K). Cycling of this gas through a CuO furnace led to complete conversion to a product gas fully condensible at 77K but recoverable in the Toepler system at dry ice temperatures, consistent with combustion of CO to CO_2. Such a reaction again demonstrates the high oxophilicity of these tantalum complexes. A similar CS_2 adduct[22] can be formed, however, it does not appear to cleanly undergo the subsequent rearrangement.



(3)

The above chemistry is formally a shoichiometric reduction of CO_2 to CO, very much resembling Mayer's[23] reaction of $(PMePh_2)_4WCl_2$ with CO_2 to yield $(PMePh_2)_2W(=O)(CO)Cl_2$. It is not clear, however, that a discrete CO_2 adduct was involved in the tungsten system, so these tantalum complexes may serve as useful models. The metal catalyzed activation of carbon dioxide is in general a difficult undertaking, although progress is being made.[24] Unfortunately, these processes are often fairly complex and mechanistic details are not always readily apparent, so that examination of model systems can help provide important insight into this desirable transformation.

Activation of organonitrile ligands. Reaction of benzyne hydride complex **1** (or other "Cp^*_2Ta-R" sources where R = H, CH_3, or CH_2Ph) with nitriles likely proceeds through some type of adduct as shown in Eq. 1. Such a species has been be observed, however, only for the case of the nitrile being trimethylsilylcyanide. This ligand is possibly bound in an η^2-fashion, as suggested by the low ν_{CN} stretch (1865 cm^{-1}) in the infrared. Dihapto nitrile complexes have been observed for molybdenum ($Cp_2Mo(NCPh)$; ν_{CN} = 1742),[25] tungsten ($Cp_2W(NCMe)$; ν_{CN} = 1725),[26] iridium ($CpIr(PPh_3)(NCAr)$; ν_{CN} = 1756-8),[27] and platinum ($(PPh_3)_2Pt(NCCF_3)$; ν_{CN} = 1734).[28] Adducts of other organonitriles are not observed under ambient conditions for this system but rather (as characterized by ^1H NMR spectroscopy) seem to be able to undergo at least two other reaction pathways, depending on the identity of the nitrile, as shown in Eqs. 4-6:

$$Cp^*_2Ta\text{-}Ph + N{\equiv}C\text{-}R \longrightarrow \underset{\mathbf{A}}{\text{"}Cp^*_2Ta(Ph)(N{\equiv}C\text{-}R)\text{"}} \qquad (4)$$

$$[Cp^*_2Ta(Ph)(N{\equiv}C\text{-}CH_2R)] \rightleftharpoons Cp^*_2Ta(Ph)(=N\text{-}CH{=}CH\text{-}R) \qquad (5)$$

R = H, C_6H_5

$$[Cp^*_2Ta(Ph)(N{\equiv}C\text{-}R)] \longrightarrow Cp^*(\eta^5\text{-}C_5Me_4\overline{CH_2})Ta(Ph)(=N\text{-}\overline{CHR}) \qquad (6)$$

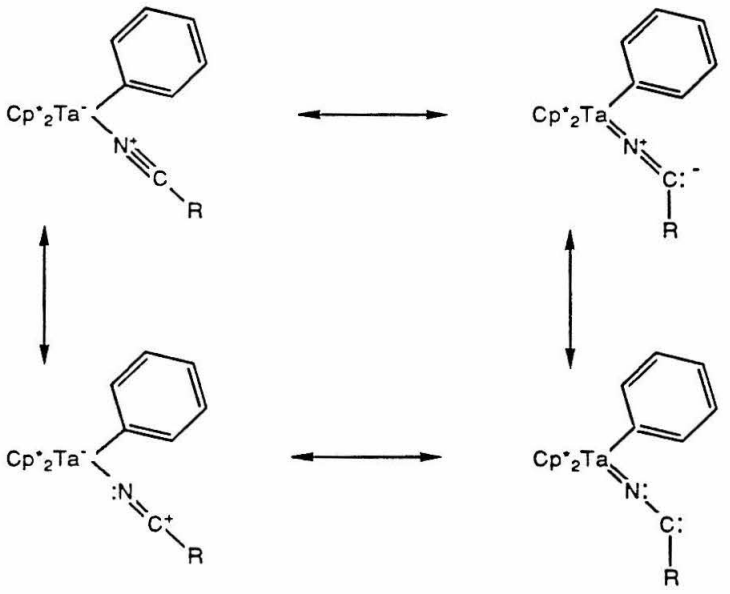
R = CH_3, $C(CH_3)_3$, CF_3, C_5H_6-4-CH_3, cyclopropyl

The net result of Eq. 5 is a 1,2-hydrogen shift although the exact mechanism is not evident. There appears to be a significant isotope dependence since the reaction with CD_3CN requires heating to proceed on according to Eq. 6 whereas in the protio case this subsequent rearrangement occurs almost immediately at room temperature. Conjugation also seems to stabilize this vinylic product since $Cp^*_2Ta(Ph)$=N-CH=CH-Ph remains unchanged even after prolonged heating at 90°C. Interestingly only the *trans*-isomer of this product (^1H NMR: $J_{NC\underline{H}=C\underline{H}Ph}$ = 13.4 Hz) is observed. The relative stability, *vis-a-vis* undergoing Eq. 6, of these species is also dependent on the nature of the alkyl group bonded to the tantalum. For

instance, the $Cp^*_2Ta(R)=N-CH=CH_2$ (R = H, CH_3, CH_2Ph) complexes appear to rearrange much less readily than the case where R = Ph.

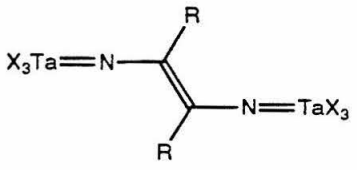
Formally the result of Eq. 6 is the addition of a C-H bond of a methyl group of the Cp* ligand across the nitrile carbon, although the exact mechanism of this transformation has not yet been determined. In the acetonitrile reaction, the CH_3 group of the nitrile remains intact, suggesting that the reaction likely proceeds *via* the adduct (**A**). There can apparently be two different isomers of the "tucked in" species although both are not always observed. The reaction with cyclopropyl cyanide leads to a "tuck in" product without ring opening. It had seemed possible that the nitrile ligand or some tautomer ($HN=C=CH_2$) could be inserting into a metalated (or "tucked in") species. Such compounds are abundant for pentamethyl-cyclopentadienyl complexes although higher temperatures are generally required for their formation. However, when $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)TaH_2$ was treated with acetonitrile, the product from the 1,2-H shift in the coordinated nitrile ligand (Eq. 5) was obtained instead of the "tuckin" product (Eq. 6). These results, along with the oxo transfer chemistry, suggest a strong driving force for the formation of tantalum heteroatom multiple bonds, leading to activation of coordinated ligand toward further reactions. No activation of other ligands other than the Cp* ligands by the nitrile has yet been observed for this system.

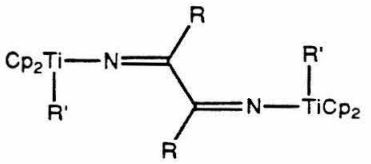
The two modes of reactivity exhibited by these compounds are reminiscent of the chemistry of organic carbenes and nitrenes.[29] For instance, substituted carbenes are known to undergo a variety of rearrangements including 1,2-shifts of hydride, alkyl, and aryl groups (carbonium ions are also known to undergo 1,2-shifts[30]). Carbenes and nitrenes also exhibit insertions into unactivated C-H bonds under mild conditions. Remembering that the permethyltantalocene fragment is very electron rich and that there is a propensity for the formation of tantalum heteroatom multiple bonds (*vide supra*), resonance forms can be readily drawn that should exhibit carbene character:



Other early transition metal systems are known to enhance carbenoid character of certain ligand systems through interactions with heteroatoms. For instance from the chemistry of η^2-acyl complexes of oxophilic metals, they have been alternatively described as having either oxycarbene[31] or carbenium[32] character.

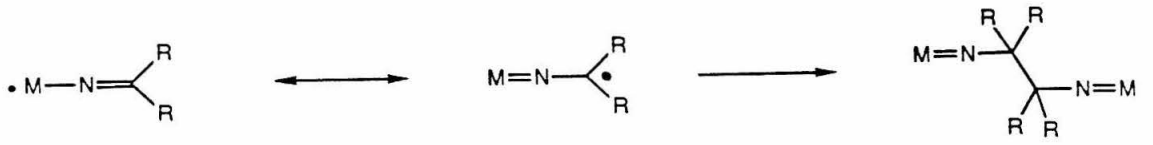
Several related systems have been reported that carry out similar activations of nitriles or imines. Tantalum (III) halide and pseudohalide complexes have been shown to react with nitriles to afford dimeric products linked through coupled nitrile ligands.[33]





Teuben[34] has observed a nitrile coupling reaction by odd electron titanocene complexes. As compared to the tantalum complexes, this reaction likely depends on a canonical form of the

nitrile adduct that has radical character at the nitrile carbon. More recently, Pedersen[35] has observed promotion of radical coupling of coordinated imines with simple niobium compounds.



Nitriles have also been shown to couple intramolecularly, either with nitriles or other unsaturated organic ligands, in [Cp^*_2M] systems.[36]

It is attractive to consider the reactivity of the permethyltantalocene-organonitrile system as deriving from an activated nitrile ligand (with enhanced carbene character) that undergoes rearrangements and insertion into unactivated C-H bonds. One disturbing observation concerning this premise is that two isomers can sometimes be observed for the final "tucked in" product (Table I). In these cases (N≡CR = N≡C-*p*-tol, N≡C-cyclopropyl) it appears that a kinetic product is formed that only slowly rearranges to the more thermodynamically stable product. These isomers likely arise from the orientation of the nitrile alkyl group (*e.g.*, whether it points into or away from the middle of the wedge). If this is indeed the case, the isomerization reaction would almost certainly require a deinsertion reaction back to the nitrile adduct (**A**) and subsequent reinsertion in the other configuration. Of course, the identity of the isomers has not been unambiguously determined so it is premature to rule out the direct pathway without further mechanistic investigation.

Methylene transfer reactions and relative α-migratory aptitudes. Treatment of **1** with phosphorus ylides (R_3P^+-CH_2^-; R = Me, Ph) results in loss of phosphine and formation of $Cp^*_2Ta(=CH_2)Ph$ (**6**); no intermediate ylide complexes are observed. The proton (δ CH_2 = 10.14) and carbon (δ CH_2 = 242.4 (t, J_{CH} = 130 Hz)) NMR data are in accord with that found for similar tantalocene complexes prepared by Schrock.[37] Thermolysis of this compound at

150°C leads to a slow first order decomposition to a complex mixture of products. If performed under a hydrogen atmosphere, this reaction is considerably cleaner, yielding only toluene and $Cp^*_2TaH_3$ at the same rate as before (Table III). These observations are consistent with a phenyl to methylene migration to afford $[Cp^*_2Ta\text{-}CH_2Ph]$ which is known to be unstable under the reaction conditions. Similar methylene transfer and alkyl to alkylidene migrations have been observed for related permethyltantalocene complexes.[38]

$$Cp^*_2Ta(=CH_2)Ph \xrightarrow[\alpha\text{-mig}]{\Delta} [Cp^*_2Ta\text{-}CH_2Ph] \xrightarrow{H_2} Cp^*_2TaH_3 + PhCH_3$$

It has been well documented in organic chemistry that aryl groups can participate in anchimeric assistance and often exhibit enhanced migratory aptitudes.[39] These properties arise from the fact that aryls can act as good bridging groups and form species like phenonium ions.[40] Such bridging interactions are expected to stabilize the transition state for the migration reactions. Fewer sets of migratory aptitudes have been determined for organometallic systems although the insertion of carbon monoxide into metal alkyl bonds, especially in $(CO)_5MnR$, has been well examined from kinetic,[41] thermodynamic,[42] and theoretical perspectives.[43] The results of these studies indicate that even though the Mn-Ph bond is stronger than Mn-R (R = Me, CH_2Ph) bonds, its migratory aptitude is comparable to or somewhat faster than for these other groups. A recent theoretical calculation[43a] indicated that the presumed transition state is greatly stabilized with the phenyl ring in a perpendicular configuration relative to the direction of migration, indicating the involvement of bridging.

Several other workers have provided strong evidence for hydride or methyl migrations to alkylidene ligands but other groups were not studied.[44] Table III lists the migration rates measured for $Cp^*_2Ta(=CH_2)R$ complexes with several different R groups. A comparison of these data indicates that phenyl is a significantly poorer migrating group than alkyl or hydride in this system. Assuming a transition state geometry similar to that for CO insertion and considering the observed ground state configuration of **6**, the conclusion is reached that the

restricted rotation of the phenyl group is likely a major factor contributing to the retardation of the migration rate. Scheme 4 graphically demonstrates the severe steric interactions that lead to the slow rotation rate. Since this is a rare example of a case in which the migration of the phenyl group is forced to proceed *via* a less favored pathway, it would be of interest to be able to perform a comparative study on a related system with decreased steric interference. Perhaps the obvious choice would be to compare the migratory aptitudes of a similar group of alkyl and aryl groups in $Cp_2Ta(=CH_2)R$ complexes. Unfortunately in this less hindered system, Schrock[37] has shown that the decomposition reactions are more complex and undergo bimolecular rearrangements deriving from the highly nucleophilic character of these carbenes. Thus such experiments must be deferred until a suitable ligand combination can be found.

SCHEME 4

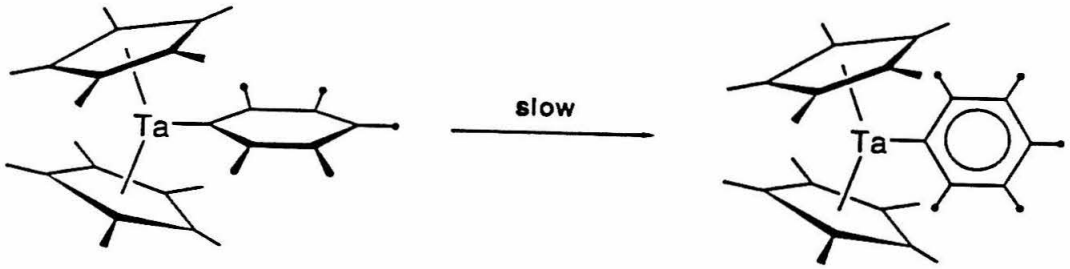


Table VI: Comparative migratory aptitudes in $Cp^*_2Ta(=CH_2)R$ complexes.

R	T(°C)	$k_1(s^{-1})$	$\Delta G^{\ddagger}(T)$	$k_1^{140\,°C}$	$\Delta G^{\ddagger}(140\,°C)$
H[a]	10	4×10^{0}	15.8	10^{4}	17
CH_3[b]	140	7.9×10^{-4}	30.3	10^{-3}	30.3
CH_2Ph[c]	120	1.3×10^{-4}	30.2	10^{-3}	30.4
Ph[d]	149	9×10^{-6}	34.7	10^{-6}	34.6

(a) Parkin, G.; Bercaw, J. E. unpublished results: extrapolated from 50 °C assuming a $\Delta S^{\ddagger}$ = -10 e.u. (b) Parkin, G.; van Asselt, A.; Bercaw, J. E. unpublished results. (c) Whinnery, L. L.; Bercaw, J. E. unpublished results: extrapolated from 120 °C using the measured $\Delta S^{\ddagger}$ = -10 e.u. (d) this work: assuming $\Delta S^{\ddagger}$ = -10 e.u.

Reactions with HX type substrates. Since $Cp^*_2Ta(=X)H$ and $Cp^*_2Ta(\eta^2\text{-}XY)H$ complexes are in equilibrium with sixteen electron, coordinatively unsaturated d^2 $Cp^*_2Ta\text{-}Z$ tautomers, they might be expected to undergo relatively facile oxidative-addition reactions. Indeed many of these compounds, especially $Cp^*_2Ta(=CH_2)H$, have proven to be useful synthetic precursors into a variety of heteroatom-containing tantalocene complexes such as $Cp^*_2Ta(=NPh)H$,[45] $Cp^*_2Ta(\eta^2\text{-}OCH_2)H$,[1b] and $Cp^*_2Ta(=O)H$.[1b] These complexes are formed because the tantalum (V) oxidative addition products seem to be unstable relative to subsequent rearrangements. For instance, Eq. 7 shows a plausible pathway for the formation of $Cp^*_2Ta(=O)H$ *via* oxidative-addition of water to $Cp^*_2Ta\text{-}Z$:

$$Cp^*_2Ta\text{-}Z + H_2O \longrightarrow [Cp^*_2Ta(Z)(H)(OH)] \longrightarrow [Cp^*_2Ta\text{-}OH]$$
$$[Cp^*_2Ta\text{-}OH] \longrightarrow Cp^*_2Ta(=O)H \qquad (7)$$

It is interesting to note that benzyne hydride complex **2** seems to show a higher selectivity with regards to the HX type substrates with which it will react than do several other tantalocene complexes like $Cp^*_2Ta(=CH_2)H$. For instance the following qualitative order of reactivity has been observed in benzene solution: RCOOH, PhOH, RSH > H_2O >> $PhNH_2$ > ROH >> RNH_2. Consideration of this behavior hints that there is a correlation between HX pK_a and the rate of its reaction with **1**. This may indicate that in this very bulky system the addition of HX may have to occur stepwise *via* a protonation reaction (except, possibly, for very small substrates). The chemistry of many of these heteroatom containing complexes have been described elsewhere and so will not be discussed here.

Reductive-elimination from $Cp^*_2Ta(H)_2(R)$ complexes. The addition of the special HX ligand dihydrogen to **1** occurs overnight at 0°C to form $Cp^*_2Ta(H)_2Ph$, **12**. ^1H NMR spectroscopy indicates that H_2 adds in the normal cis-fashion such that the hydride ligands

occupy inequivalent sites on the metal center and appear as two doublets at δ 0.95 and 3.71. The coupling constant ($^2J_{HH}$) of 11 Hz is virtually identical to that found for $Cp^*_2TaH_3$.[1a] No other *cis* alkyl hydride complexes of the Group V metallocenes have been observed except for the metallacyclic compounds $Cp^*_2Ta(C_6H_4\text{-}o\text{-}CH_2)H$ and $Cp^*_2Ta(CH_2\text{-}C_6H_4\text{-}o\text{-}CH_2)H$,[46] although hydrogenolysis and H/D exchange reactions have been observed that are proposed to proceed *via* such intermediates.[47]

At room temperature, **12** undergoes a clean first order reductive elimination of benzene to afford either $Cp^*(\eta^5,\eta^1\text{-}C_5Me_4CH_2)TaH_2$ or $Cp^*_2TaH_3$ (if there is excess hydrogen present to trap the Cp^*_2TaH initially formed). The rate (Table IV, Figure 4) of this reaction has been measured to be: $k^{23\,°C} = 3.15(5)\times10^{-5}\ s^{-1}$, $\Delta G^{\ddagger}(23\,°C) = 23.42(5)\ kcal\cdot mol^{-1}$. The rate does not appear to depend on the presence or absence of hydrogen and seems to be a simple reductive elimination reaction. Tractable alkyl hydride species that allow direct study of reductive eliminations are quite rare, the only examples being $Cp^*Rh(PMe_3)(R)H$,[48] $Cp^*Ir(PMe_3)(R)H$,[49] $(PPh_3)_2Pt(R)H$,[50] $(Cy_2PCH_2CH_2PCy_2)Pt(R)H$,[51] $Cp^*_2Zr(R)H$,[52] and $(C_5X_5)_2W(R)H$ (X = H,[53] Me[54]). Treatment of $Cp^*_2Ta(=CH_2)H$ or $Cp^*_2Ta(=CHPh)H$, which are in equilibrium with $[Cp^*_2TaCH_3]$ and $[Cp^*_2TaCH_2Ph]$ respectively, with hydrogen leads to alkane and $Cp^*_2TaH_3$ but no alkyl dihydride species are observed. A lower limit for the rate of reductive-elimination from $Cp^*_2Ta(CH_2Ph)H_2$ can be estimated from the rate of disappearance ($k \approx 8\times10^{-4}\ s^{-1}$) of $Cp^*_2Ta(=CHPh)H$ when it is treated with hydrogen gas at room temperature (Table IV). Thus it appears that reductive elimination of benzene is less facile than of other hydrocarbons in this system.

Several studies of elimination of RX from M(R)X species (X = alkyl, vinyl, aryl, and acyl) have shown a general trend for increased reaction rates when one of the leaving groups is bonded through an sp^2 carbon.[55] It has been proposed that the π-systems of these ligands can coordinate in the course of the reductive elimination reaction (or the converse, C-H oxidative addition) and thus help to stabilize the transition state.[56] Relative rates for only a very

Table VII. Reductive-elimination rates from $Cp^*_2Ta(R)(H)_2$ complexes.

Cmpd	T (°C)	k_{RE} (s^{-1})	$\Delta G^{\ddagger}(T)$ (kcal · mol^{-1})
$Cp^*_2Ta(Ph)(H)_2$	23	$3.15(5)\times10^{-5}$	23.42(5)
$Cp^*_2Ta(Ph)(D)_2$	23	$2.12(5)\times10^{-5}$	23.65(5)
$Cp^*_2Ta(Ph)(H)_2$	26	$5.0(3)\times10^{-5}$	23.4(1)
$Cp^*_2Ta(Ph)(H)_2$	35	$1.45(10)\times10^{-4}$	23.46(10)
$Cp^*_2Ta(CH_2Ph)(H)_2$	25	$> 8.0\times10^{-4}$	< 21.7

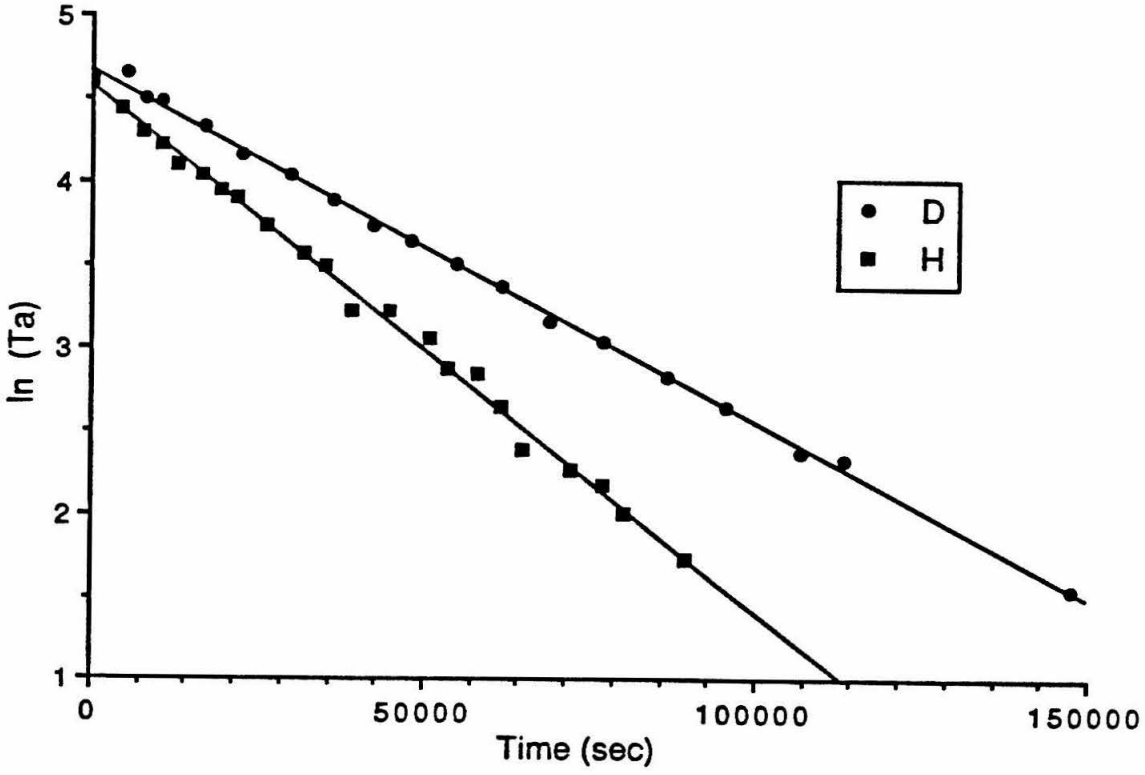


Figure 4. Kinetic plots for reductive elimination of benzene from $Cp^*_2Ta(H)_2Ph$ (■ k = 3.15(5) x 10^{-5} s^{-1}; R = 0.998) and $Cp^*_2Ta(D)_2Ph$ (•; k = 2.12(5) x 10^{-5} s^{-1}; R = 0.999) at 23 °C in C_6D_6.

Table VIII. Some observed deuterium isotope effects for reductive elimination from metal alkyl hydride and metal dihydride species.

System	k_H/k_D	T(°C)	reference
$Cp^*(PMe_3)Rh(CH_2CH_3)H$	0.50(1)	-30	a
$Cp^*(PMe_3)Ir(c\text{-}C_6H_{11})H$	0.70(1)	130	b
$Cp^*_2W(CH_3)H$	0.70(7)	100	c
$(Cy_2PCH_2CH_2PCy_2)Pt(CH_2CMe_3)H$	1.5	69	d
$(PPh_3)_2Pt(CH_2CF_3)H$	2.2	40	e
$(PPh_3)_2Pt(CH_3)H$	3.3(3)	-25	f
$(PMe_3)_2PtH_2$	0.72(6)	21	g
$[(PPh_3)_2Ir(nbd)H_2]^+$	0.4(2)	25	h
$[(PMePh_2)_2Ir(CO)_2H_2]^+$	2.1(3)	20	i

(a) Periana, R.A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332-46. (b) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537-50. (c) Parkin, G.; Bercaw, J. E. manuscript in preparation. (d) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436-48. (e) Michelin, R. A.; Faglia, S.; *Inorg. Chem.* **1983**, *22*, 1831-4. (f) Halpern. J. *Acc. Chem. Res.* **1982**, *15*, 332-8 and references therein. (g) Packett, D. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 5036-8. (h) Howarth, O. W.; McAteer, C. H.; Moore, C. H.; Morris, G. E. *J. Chem. Soc., Dalton Trans.* **1984**, 1171-80. (i) Mays, M. J.; Simpson, R. N. F.; Stefanini, F. P. *J. Chem. Soc. (A)*, **1970**, 3000-2.

few series of corresponding alkyl hydride complexes have been measured and general trends are less apparent. Experiments have been reported in which aryl groups can eliminate either more rapidly[57] or less rapidly[58] than other alkyl groups. In this latter case, the course of the reaction is almost certainly determined by thermodynamic effects as M-Ar bonds are generally thought to be considerably stronger than other M-R bonds.[59]

Many (but not all) alkyl hydride and dihydride reductive elimination reactions exhibit inverse deuterium isotope effects (Table V). These inverse effects have been rationalized in terms of a preequilibrium with an unobserved intermediate, proposed to be a C-H or H-H "σ-complex", which has increased zero-point energy relative to the starting complex.[48] A normal kinetic deuterium isotope effect of 1.5(1) was measured (Table IV) for the decomposition of $Cp^*_2Ta(D)_2Ph$ at 23°C. This observation could imply that this system is sufficiently crowded

so as to preclude a strong Ph-H interaction with the tantalum center. The lack of an inverse isotope effect is not sufficient evidence, however, to rule out the intermediacy of the σ-complex since the position of such a species, relative to the transition state for the elimination reaction, is important in determining whether the inverse effect is observed.[54]

CONCLUSIONS

The electron-rich permethyltantalocene fragment, which had previously been shown to stabilize a wide variety of unsaturated organic moieties, can also form a very stable benzyne hydride complex. While several examples of transition metal benzyne complexes have been prepared and studied, **1** is the first isolated benzyne hydride. Moreover, this compound undergoes a rapid and reversible β-migratory insertion reaction in an equilibrium with a coordinatively unsaturated phenyl tautomer. This behavior has allowed mechanistic study of the benzyne insertion reaction, a process that has been proposed but never before directly observed.

The high reactivity of the sixteen electron phenyl tautomer makes **1** a useful synthetic precursor for a wide variety of phenyl permethyltantalocene compounds. Due to steric interactions with the bulky Cp* ligands, these compounds exhibit high rotational barriers (> 21 kcal $\cdot$ mol^{-1}) about the Ta-Ph bond. We have demonstrated that this hindered rotation can greatly affect the chemistry (*e.g.*, migration reactions) of metal aryl moieties by preventing the aromatic π-system from being involved in the reaction coordinate. Because of the diversity of $Cp^*_2Ta(L)Ph$ complexes that we have been able to prepare, it has been possible to examine several types of fundamental organometallic reactions (reductive elimination, migratory insertion, *etc.*) involving metal aryl bonds, an area that has not been greatly explored.

Table I. ^{1}H NMR data for tantalocene benzyne and phenyl complexes.

Compound	Assignment[a]	δ/PPM (multiplicity)	Coupling/Hz
$Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$[b]	η^5–$C_5(CH_3)_5$	1.62 (s)	
	H_2	2.24 (s,br)	
1	H_3	8.05 (d)	5.5
	H_4, H_5	7.46 (m)	
	H_6	7.92 (d)	5.5
$Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$[c]	η^5–$C_5(CH_3)_5$	1.65 (s)	
	H_2	1.96 (s,br)	
	H_3	7.61 (d)	6.0
1	H_4	7.00 (≈t)	6.5
	H_5	7.04 (≈t)	6.4
	H_6	7.48 (d)	6.2
$Cp^*_2Ta(\eta^2\text{-}C_6H_3\text{-}4\text{-}CH_3)H$[c]	η^5–$C_5(CH_3)_5$	1.65 (s)	
	CH_3	2.28 (s)	
	H_2	1.94 (s,br)	
2	H_3	7.28 (s)	
	H_5	6.90 (d)	6.3
	H_6	7.51 (d)	6.3
$Cp^*Cp^{\phi}Ta(\eta^2\text{-}C_6H_4)H$[b]	η^5–$C_5(CH_3)_5$	1.52 (s)	
	η^5–$C_5(CH_3)_4Ph$	1.88 (s)	
		1.84 (s)	
		1.71 (s)	
		1.19 (s)	
4	η^5–$C_5(CH_3)_4(C_6H_5)$	7.72 (d)	7.4
		7.32 (≈t)	7.6
		≈7.13	
	H_2	2.60 (s)	
	H_3	8.05 (d)	4.9
	H_4,H_5	7.6 (m)	
	H_6	8.03 (d)	5.6
$Cp^*_2Ta(=CH_2)C_6H_5$[c]	η^5–$C_5(CH_3)_5$	1.75 (s)	
	$=CH_2$	9.75 (s)	
	H_2	7.06 (d)	7.0
6	H_3	6.62 (≈t)	7
	H_4	6.71 (≈t)	7
	H_5	6.85 (≈t)	7
	H_6	6.67 (d)	7.2
$Cp^*_2Ta(CO)C_6H_5$[b]	η^5–$C_5(CH_3)_5$	1.52 (s)	
	H_2	8.03 (d)	7.0
7	H_6	6.95 (d)	7.9
	H_3,H_4,H_5	7.0-7.2 (m)[d]	

Compound	Assignment	δ/PPM (multiplicity)	Coupling/Hz
$Cp^*_2Ta(CNCH_3)C_6H_5$[b]	η^5–$C_5(CH_3)_5$	1.59 (s)	
	CH_3	3.37 (s)	
	H_2	8.21 (d)	7.8
8	H_4	7.08 (≈t)	7.2
	H_6	7.03 (d)	7.5
	H_3,H_5	7.1-7.2 (m)[d]	
$Cp^*_2Ta(=O)C_6H_5$[b]	η^5–$C_5(CH_3)_5$	1.71 (s)	
	H_2	7.89 (d)	7.4
9	H_6	6.90 (d)	7.4
	H_3,H_4,H_5	7.1-7.3 (m)[d]	
$Cp^*_2Ta(O_2)C_6H_5$[b]	η^5–$C_5(CH_3)_5$	1.54 (s)	
	H_2	8.16 (d)	7.7
	H_3	7.50 (td)	7.5, 1.4
10	H_5	7.29 (td)	7.4, 1.4
	H_4,H_6	7.1-7.2 (m)[d]	
$Cp^*_2Ta(CO_2)C_6H_5$[c]	η^5–$C_5(CH_3)_5$	1.61 (s)	
	H_2	7.70 (d)	7.5
	H_3	7.19 (≈t)	7.5
11	H_4	6.92 (≈t)	7.0
	H_5	7.08 (≈t)	7.2
	H_6	7.33 (d)	7.5
$Cp^*_2Ta(CS_2)C_6H_5$[b]	η^5–$C_5(CH_3)_5$	1.45 (s)	
	H_2	8.59 (d)	7.7
	H_3,H_4,H_5,H_6	7.1-7.4 (m)[d]	
$Cp^*_2Ta(H)_2C_6H_5$[b]	η^5-$C_5(CH_3)_5$	1.70 (s)	
	Ta-H	2.71 (d)	12
12		0.95 (d)	12
	H_2	8.51 (d)	7.3
	H_3,H_4,H_5,H_6	7.1-7.3 (m)[d]	
$Cp^*_2Ta(N{\equiv}CSi(CH_3)_3)C_6H_5$[b]	η^5-$C_5(CH_3)_5$	1.72 (s)	
	η^5-$C_5(CH_3)_4CH_2$	1.93 (s)	
		1.70 (s)	
		1.52 (s)	
		1.31 (s)	
	η^5-$C_5(CH_3)_4CH_2$	2.81 (dd)	7.6, 12.8
		2.69 (dd)	9.8, 12.8
	$=NCHSi(CH_3)_3$	5.86 (dd)	7.6, 9.8
	$=NCHSi(CH_3)_3$	0.24 (s)	
	C_6H_5	7.98 (d)	

Compound	Assignment	δ/PPM (multiplicity)	Coupling/Hz
$Cp^*_2Ta(=NCD=CD_2)C_6H_5$[e]	η^5-$C_5(CH_3)_5$	1.72 (s)	
	C_6H_5	7.76 (d)	
		6.8-7.4[d]	
$Cp^*_2Ta(=NCH=CHPh)C_6H_5$[e]	η^5-$C_5(CH_3)_5$	1.68 (s)	
	=N-CH=CHC_6H_5	8.23 (d)	13.4
	=N-CH=CHC_6H_5	5.44 (d)	13.4
	=N-CH=CHC_6H_5	6.8-7.4	
	C_6H_5	7.73 (d)	7.9
		6.8-7.4[d]	
$Cp^*_2Ta(=NCH=CH_2)CH_3$[e]	η^5-$C_5(CH_3)_5$	1.78 (s)	
	CH_3	0.20 (s)	
	=N-CH=CH_2	7.31 (dd)	8.0, 14.9
	=N-CH=CH_2	3.99 (dd)	2.1, 14.9
		3.67 (dd)	2.1, 8.0
$Cp^*(\eta^5$-$C_5Me_4\overline{CH_2})Ta(=N\overline{CHMe})Ph$[e]	η^5-$C_5(CH_3)_5$	1.74	
	η^5-$C_5(CH_3)_4CH_2$	1.91	
		1.67	
		1.49	
		1.26	
	η^5-$C_5(CH_3)_4CH_2$	2.85 (dd)	6.8, 13.2
		2.30 (dd)	7.8, 13.2
	=NC$H$$CH_3$	5.94 (≈ sextet)	7
	=NCHCH_3	1.33 (d)	6.6
	H_2	8.01 (d)	
	H_6	7.41 (d)	
	H_3-H_5	7.1-7.3[d]	
$Cp^*(\eta^5$-$C_5Me_4\overline{CH_2})Ta(=N\overline{CHCD_3})Ph$[b]	η^5-$C_5(CH_3)_5$	1.75 (s)	
	η^5-$C_5(CH_3)_4CH_2$	1.92 (s)	
		1.68 (s)	
		1.49 (s)	
		1.26 (s)	
	η^5-$C_5(CH_3)_4CH_2$		
	=NC$H$$CD_3$	5.93 (≈t)	7.5
	C_6H_5	[d]	

Compound	Assignment	δ/PPM (multiplicity)	Coupling/Hz
Cp*(η^5-$C_5Me_4\overline{CH_2}$)Ta(=N$\overline{CHCF_3}$)Ph[e]	η^5-$C_5(CH_3)_5$	1.66	
	η^5-$C_5(CH_3)_4CH_2$	1.68	
		1.57	
		1.39	
		1.18	
	η^5-$C_5(CH_3)_4CH_2$	2.83 (m)	
	=NC*H*CF_3	5.92 (m)	
	C_6H_5	7.93 (d)	7.3
		6.78 (d)	7.1
		7.1-7.3[d]	
Cp*(η^5-$C_5Me_4\overline{CH_2}$)Ta(=N$\overline{CHCMe_3}$)Ph[b]	η^5-$C_5(CH_3)_5$	1.72	
	η^5-$C_5(CH_3)_4CH_2$	1.94	
		1.66	
		1.53	
		1.30	
	η^5-$C_5(CH_3)_4CH_2$	2.79 (dd)	6.8, 12.9
		2.53 (dd)	9.8, 12.9
	=NC*H*$C(CH_3)_3$	5.38 (dd)	6.8, 9.8
	=NCHC(CH_3)$_3$	1.09 (s)	
	C_6H_5	8.10 (d)	7.3
		6.90 (d)	8.6
		7.1-7.3[d]	
Cp*(η^5-$C_5Me_4\overline{CH_2}$)Ta(=N$\overline{CH}$-tol)Ph[e]	η^5-$C_5(CH_3)_5$	1.72 (s)	
	η^5-$C_5(CH_3)_4CH_2$	1.93 (s)	
isomer 1		1.70 (s)	
		1.52 (s)	
		1.31 (s)	
	η^5-$C_5(CH_3)_4CH_2$		
	=NC*H*-C_6H_4-*p*-CH_3		
	=NCH-C_6H_4-*p*-C*H*$_3$	2.21 (s)	
	=NCH-C_6H_4-*p*-CH$_3$		
	C_6H_5	d	
Cp*(η^5-$C_5Me_4\overline{CH_2}$)Ta(=N$\overline{CH}$-tol)Ph[e]	η^5-$C_5(CH_3)_5$	1.76 (s)	
	η^5-$C_5(CH_3)_4CH_2$	1.97 (s)	
isomer 2		1.69 (s)	
		1.49 (s)	
		1.18 (s)	
	η^5-$C_5(CH_3)_4CH_2$		
	=NC*H*-C_6H_4-*p*-CH_3		
	=NCH-C_6H_4-*p*-C*H*$_3$	2.23 (s)	
	=NCH-C_6H_4-*p*-CH$_3$		
	C_6H_5	d	

Compound	Assignment	δ/PPM (multiplicity)	Coupling/Hz
$Cp^*(\eta^5\text{-}C_5Me_4\overline{CH_2})Ta(=\overline{NCH}\text{-}c\text{-}C_3H_5)Ph$[b]	$\eta^5\text{-}C_5(CH_3)_5$	1.75 (s)	
	$\eta^5\text{-}C_5(CH_3)_4CH_2$	1.87 (s)	
isomer 1		1.68 (s)	
		1.50 (s)	
		1.29 (s)	
	$\eta^5\text{-}C_5(CH_3)_4CH_2$	2.95 (dd)	13.2, 7
		2.62 (dd)	13.5, 8
	=NC*H*-cp	5.02 (≈q)	≈7.8
	=NCH-cp	0.2-1.2	
	C_6H_5	8.08 (d)	8.2
		6.96 (d)	7.2
		7.1-7.3[d]	

(a) See Scheme 1 and Figure 3 for numbering schemes.
(b) Measured in d_6-benzene on a Bruker AM-500 NMR spectrometer.
(c) Measured in d_8-dioxane on a Bruker AM-500 NMR spectrometer.
(d) The phenyl region was not well enough resolved to make definite assignments.
(e) Measured in d_6-benzene on a Jeol GX-400 NMR spectrometer.

Table II. ^{13}C NMR data for tantalocene benzyne and phenyl complexes.

Compound	Assignment	δ/PPM (multiplicity)	Coupling/Hz
$Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$[a]	η^5–$C_5(CH_3)_5$	107.9 (s)	
	η^5–$C_5(CH_3)_5$	11.8 (q)	126
	C_1,C_2	158.9 (s,br)	
1		157.2 (s,br)	
	C_3-C_6	131.8 (d)	158
		129.8 (d)	151
		129.5 (d)	154
		127.1 (d)	155
$Cp^*_2Ta(=CH_2)C_6H_5$[b]	η^5–$C_5(CH_3)_5$	110.7 (s)	
	η^5–$C_5(CH_3)_5$	12.0 (q)	127
	$=CH_2$	242.4 (t)	130
6	C_1	180.9 (s)	
	C_2-C_6	155.9 (d)	161
		141.7 (d)	153
		127.4 (d)	154
		125.1 (d)	155
		122.7 (d)	157
$Cp^*_2Ta(CO)C_6H_5$[c,d]	η^5-$C_5(CH_3)_5$	100.8	
	η^5-$C_5(CH_3)_5$	11.0	
	CO	268.0	
7	C_1	169.2	
	C_2-C_6	150.0	
		144.7	
		122.8	
		127.3	
		125.8	
$Cp^*_2Ta(CNCH_3)C_6H_5$[c]	η^5-$C_5(CH_3)_5$	103.6 (s)	
	η^5-$C_5(CH_3)_5$	11.4 (q)	127
	$CNCH_3$	288.1 (s)	
8	$CNCH_3$	37.3 (q)	138
	C_1	174.0 (s)	
	C_2-C_6	153.4 (dt)	157,7.8
		143.9 (dt)	151.7.6
		122.6 (dt)	157,7.3
		127.1 (d)	≈156
		125.6 (d)	154

(a) Measured in d_8-THF at 100 MHz on a Jeol GX-400 NMR spectrometer.
(b) Measured in d_8-dioxane at 100 MHz on a Jeol GX-400 NMR spectrometer.
(c) Measured in d_6-benzene at 100 MHz on a Jeol GX-400 NMR spectrometer.
(d) Decoupled spectrum.

EXPERIMENTAL

General Considerations. All air sensitive manipulations were carried out using glove box or high vacuum line techniques. Solvents were dried over CaH_2 or sodium benzophenone and stored over titanocene. Benzene-d_6 and toluene-d_8 were dried over activated 4 Å molecular sieves and stored over titanocene. 1,4-dioxane-d_8 was also dried over sieves but stored over sodium benzophenone. Argon was purified by passage over MnO on vermiculite and activated molecular sieves.

NMR Spectra were recorded on Varian EM-390 (^{1}H, 90 MHz), JEOL FX90Q (^{1}H, 89.56 MHz; ^{13}C, 22.50 MHz), JEOL GX400Q (^{1}H, 399.78 MHz; ^{13}C, 100.38 MHz) and Bruker AM500 (^{1}H, 500.13 MHz) spectrometers. Infrared spectra were recorded on a Beckman 4240 spectrometer and peak positions are reported in cm^{-1}. Mass spectra and elemental analyses were conducted by L. Henling or F. Harvey of the Caltech Analytical Laboratory.

Starting materials. Aryl lithiums were prepared by the reaction of the aryl bromides with butyl lithium and isolated as the solid salts.[60] $Me_3P{=}CH_2$ was prepared by deprotonation of $[Me_4P][Br]$.[61] $Cp^*_2TaCl_2$ was prepared as previously described.[1a] Hydrogen and deuterium gases were purified by passage over MnO on vermiculite and activated molecular sieves.

$Cp^*_2Ta(\eta^2\text{-}C_6H_4)H$ (1). $Cp^*_2TaCl_2$ (2.2 g, 4.1 mmole) and solid Li-C_6H_5 (0.84 g, 10 mmole) were weighed into a frit assembly and 40 mL of toluene condensed in at -78°C. This slurry was allowed to warm to room temperature (slight warming may increase the yield) and to stir overnight (12-18 hrs), resulting in a red-brown solution. This solution was filtered to remove the lithium salts, the solvent removed under reduced pressure, and biphenyl removed by sublimation (warm water bath). Extraction of the resulting brown solid into pentane, concentration, and cooling to -78°C afforded 1 as a tan microcrystalline solid (1.6 g, 73% yield).

IR (nujol): 1808, 1742, 1569, 1418, 1345, 1297, 1145, 1028, 744. Mass spectrum (m/e): 528 (M^+), 450, 154 (Ph-Ph). Anal. Calcd. for $C_{26}H_{35}Ta$: C, 59.09; H, 6.68. Found: C, 59.27; H, 6.47.

$Cp^*_2Ta(\eta^2\text{-}C_6H_3\text{-}4\text{-}CH_3)H$ (2). $Cp^*_2TaCl_2$ (1.4 g, 2.7 mmole) and solid *p*-tolyl lithium (0.675 g, 6.9 mmole) were heated in 25 mL of toluene at 60-80°C for 6 hrs. Workup as above for **1** afforded 0.94 g (65% yield) of brown microcrystalline **2**. Anal. Calcd. for $C_{27}H_{37}Ta$: C, 59.77; H, 6.87. Found: C, 59.83; H, 6.66.

$Cp^*_2Ta(\eta^2\text{-}C_6H_3\text{-}3\text{-}CH_3)H$ (3a) / $Cp^*_2Ta(\eta^2\text{-}C_6H_3\text{-}5\text{-}CH_3)H$ (3b). $Cp^*_2TaCl_2$ (1 g, 1.9 mmole) and solid *p*-tolyl lithium (0.6 g, 6 mmole) were reacted in 20 mL of toluene as for **1** above. Workup of the very soluble material from a minimum of pentane afforded 214 mg (21% yield) of a brown microcrystalline mixture of **3a/3b**. Mass spectrum (m/e): 542 (M^+), 450, 182 ($Me\text{-}C_6H_4\text{-}C_6H_4\text{-}Me$) Anal. Calcd. for $C_{27}H_{37}Ta$: C, 59.77; H, 6.87. Found: C, 58.84; H, 6.51.

$Cp^*(\eta^5\text{-}C_5Me_4Ph)Ta(\eta^2\text{-}C_6H_4)H$ (4). A suspension of $Cp^*Cp^{\phi}TaCl_2$ (109 mg, 0.19 mmole) and phenyl lithium (50 mg, 0.6 mmole) in toluene (8 mL) was stirred overnight (16 hrs) at room temperature. This mixture was then stirred for another 5 hrs at 50°C to yield a dark orange solution which was pumped to dryness on the vacuum line. Extraction into pentane and evaporation of solvent led to 66 mg (60% yield) of oily **4**. Anal. Calcd. for $C_{27}H_{37}Ta$: C, 63.05; H, 6.32. Found: C, 63.84; H, 6.27.

$Cp^*_2Ta(=CH_2)C_6H_5$ (6). A solution of **1** (515 mg, 0.96 mmole) and $Me_3P{=}CH_2$ (0.12 mL, 1.07 mmole) in toluene were heated in a glass bomb at 80°C for 12 hrs. After removing the volatiles under reduced pressure, the resulting brown solid was extracted into toluene, filtered, and concentrated. This solution was diluted with pentane and slowly cooled to -78°C to afford 200 mg (39% yield) of microcrystalline brown **6**. Mass spectrum (m/e): 542 (M^+), 528, 450. Anal. Calcd. for $C_{27}H_{37}Ta$: C, 59.77; H, 6.87. Found: C, 59.60; H, 6.71.

$Cp^*_2Ta(CO)C_6H_5$ (7). A solution of **1** (170 mg, 0.32 mmole) and excess CO were reacted for 24 hrs in 10 mL of toluene in a glass bomb. The toluene was removed under

reduced pressure and the resulting solid extracted into petroleum ether. Filtration and removal of solvent *in vacuo* yielded 110 mg (62 % yield) of brown powder. IR (C_6D_6, CaF_2): 3040, 2975, 2958, 2899, 2853, 1850(vs), 1564, 1491, 1467, 1420, 1379. Anal. Calcd. for $C_{27}H_{35}OTa$: C, 58.27; H, 6.34. Found: C, 58.28; H, 6.34.

$Cp^*_2Ta(CNCH_3)C_6H_5$ (8). A solution of **1** (1.55 mg, 0.29 mmole) and excess $CNCH_3$ (60 torr in 500 mL at 25°C, 1.5 mmole) were stirred overnight (12 hrs) in 10 mL of petroleum ether at 25°C, yielding a red solution. Removal of the volatiles and workup (extraction, concentration, and cooling to -78°C) from hexamethyldisiloxane afforded 90 mg (54% yield) of red-brown microcrystalline solid. IR (C_6D_6, CaF_2): 3039, 2987, 2958, 2901, 2852, 1881, 1759 (ν_{CN}), 1377.

$Cp^*_2Ta(=O)C_6H_5$ (9). A solution of **11** (285 mg, 0.5 mmole) in toluene was thermolyzed at 110°C for 40 hrs. Workup from pentane afforded 150 mg (55 % yield) of brown microcrystalline solid. IR (nujol): 3045, 1018, 856($\nu_{Ta=O}$), 730, 708. Anal. Calcd. for $C_{26}H_{35}OTa$: C, 57.35; H, 6.48. Found: C, 57.34; H, 6.42.

$Cp^*_2Ta(\eta^2\text{-}O_2)C_6H_5$ (10). A solution of **1** (360 mg, 0.68 mmole) in 20 mL of toluene was stirred under a dry oxygen atmosphere leading to an orange solution. This solution was filtered and concentrated to an oil. Addition of petroleum ether resulted in a tan precipitate which isolated and washed with petroleum ether to afford 307 mg (80 % yield) of **10**. IR (nujol): 3057, 3037, 1485, 872($\nu_{O\text{-}O}$), 732, 707. Mass spectrum (m/e): 560 (M^+), 544, 528 (1^+), 466, 450, 427, 350. Anal. Calcd. for $C_{26}H_{35}O_2Ta$: C, 55.71; H, 6.29. Found: C, 55.39; H, 5.99.

$Cp^*_2Ta(CO_2)C_6H_5$ (11). A solution of **1** (307 mg, 0.58 mmole) and CO_2 (150 torr in 350 mL at 25°C, 2.8 mmole) were heated in 10 mL of toluene for 18 hrs in a glass bomb, resulting in a green solution. This solution was filtered and concentrated to an oil. Addition of pentane at -78°C resulted in the precipitation of **11** as a green microcrystalline solid (205 mg, 62% yield). δ ($^{13}CO_2$) = 215.1. IR (nujol): 3032, 1699 ($\nu_{C=O}$), 1568, 1483, 1134, 1022, 749, 731, 737. Anal. Calcd. for $C_{27}H_{38}O_2Ta$: C, 56.64; H, 6.16. Found: C, 56.47; H, 6.02.

$Cp^*_2Ta(CS_2)C_6H_5$. A solution of 1 (185 mg, 0.35 mmole) and CS_2 (60 torr in 500 mL at 25°C, 1.6 mmole) were stirred for 3 hrs in 10 mL of petroleum ether leading to a red-brown precipitate. The volatiles were removed and the resulting solid extracted into toluene and concentrated to a thick oil. Addition of pentane at -78°C resulted in precipitation of brown-red powder (112 mg, 53% yield). IR (nujol): 3040, 1569, 1483, 1416, 1118, 1088 ($\nu_{C=S}$), 1050(w), 1018, 730, 706. Anal. Calcd. for $C_{27}H_{38}S_2Ta$: C, 53.63; H, 5.83. Found: C, 53.97; H, 5.67.

Measurement of migratory insertion rates using coalescence and magnetization transfer techniques. A typical sample was prepared in a glove box by loading the complex (≈30 mg) and benzene-d_6 (0.4 mL) in a sealable NMR tube. Tubes were sealed at -78°C under 700 torr argon. The temperature was measured by the peak separation of an ethylene glycol sample. The sample temperature was maintained by the NMR's (Bruker AM-500) variable temperature unit and were determined to be constant to within ±1°C. The room temperature ^1H NMR spectrum was recorded before and after the experiment; no decomposition was evident. The rate of exchange at the coalescence temperature was calculated using the Gutowsky-Holm approximation, $k_{exchange}(T_c) = (\pi/\sqrt{2})\Delta\nu$,[62] where $\Delta\nu$ is the frequency separation between the peaks in the room temperature spectrum. The rate of insertion in these cases is related to the exchange rate by a factor of two: $k_1(T_c) = 2k_{exchange}(T_c) = \sqrt{2}\pi\Delta\nu$. $\Delta G^{\ddagger}(T_c)$ can be calculated from the Eyring Equation, $\Delta G(T_c) = RT_c\ln(\kappa kT_c/k_c h)$,[63] assuming a transmission coefficient, κ, of 1.

Relaxation times (T_1) of all exchanging signals were measured at each temperature by an inversion recovery pulse sequence and analyzed by a three-parameter fitting routine. Magnetization transfer experiments were performed by selectively inverting one of the exchanging signals with a single decoupler pulse and then waiting a variable delay time (τ) before executing the observation pulse ($\pi/2$). Measurements were generally made for 15-20 τ values spanning a range from milliseconds to several times the T_1 values. The spectrometer's automatic integration routine was used to obtain lists of the peak areas. Peak intensities were

determined as ratios of the areas of the exchanging resonances to a constant resonance. A four parameter nonlinear least-squares fit of the differences of the inverted resonance and the exchanging resonance as a function of delay time to the magnetization equation was performed using a version of the computer program written by Perkin.[64] Errors in k_1 were propagated from the standard deviation calculated for $k_{exchange}$ by the curve-fitting routine.

Measurement of thermolysis rate constants. Samples were prepared as described above for the magnetization transfer experiments. The tubes were maintained in a constant temperature bath (± 1 °C) and periodically removed for a measurement. Typical measurements were performed by comparing the peak heights obtained on a Varian EM-390 NMR spectrometer with those of an added standard (typically ferrocene). The kinetics were monitored and found to be linear over a period of at least three half-lives.

Measurement of reductive elimination rate constants from 12. Sealable NMR tubes were charged with ≈30 mg of **1** and 0.4 mL d_8-toluene in a glove box. These tubes were then sealed under 700 torr H_2 (or D_2) at -196 °C and allowed to react at 0 °C overnight to generate the dihydride complexes. The kinetics of the decomposition reactions were monitored as described above.

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CHAPTER 3

Synthesis and Reactivity of Cationic (d^0) and Anionic (d^2) Permethyltantalocene Compounds Derived from Paramagnetic d^1 $Cp^*_2TaX_2$ (X = Halide, Alkyl, and Hydride) Complexes.

Abstract: The series of paramagnetic $Cp^*_2TaX_2$ (X = chloride, methyl, and hydride) complexes show well behaved electrochemical oxidations and reductions. Stable anionic compounds $[Cp^*_2TaY_2]^-$ (Y = CH_3, H) are obtained by reduction with Na/K in THF, and stable cationic complexes $[Cp^*_2TaX_2]^+$ can be isolated after oxidation with silver salts. These ionic species may be considered charged analogs to well known Group IV and Group VI complexes. The dimethyl compounds display some interesting acid-base chemistry leading to interconversions between cationic, anionic, and alkylidene species. Thermal decompositions (generally involving 1,2-elimination) and some reaction chemistry with various substrates (CO, RC≡N, NO, RX, *etc.*) are described for the neutral and cationic methyl complexes.

INTRODUCTION

A sizeable body of information has now been compiled on the chemistry of the bent metallocenes of the early transition series. In particular, those complexes of the Group IV (Ti, Zr)[1] and Group VI (Mo, W)[2] metals have exhibited a rich array of "simple" compounds with exciting reactivity. For instance, many studies have been performed just on hydride, alkyl, and halide complexes. While the study of these families of compounds has flourished, the study of paramagnetic and charged complexes of the early transition metals has only recently achieved more than passing interest. The study of diamagnetic organometallics has depended on the powerfully diagnostic technique of NMR spectroscopy. The tools for examining paramagnetic materials (*e.g.* EPR spectroscopy and magnetic susceptibility) are much less easily applied to routine characterization and structure identification. Charged species are generally more difficult to work with because they invariably require polar solvents and reactive (with regards to most organometals) counterions, both of which can lead to severe complications.

Having been interested in the chemistry of Group V metallocene complexes (especially those of permethyltantalocene), we decided to examine some of the chemistry of the 17 electron complexes $Cp^*_2TaCl_2$ and $Cp^*_2Ta(CH_3)_2$. Comparison of paramagnetic dialkyl metallocenes with the 16 electron Group IV and 18 electron Group VI compounds already known would be useful for defining the roles of odd electron species in organometallic chemistry. Preliminary electrochemical experiments had also indicated that cationic and anionic $Cp^*_2TaR_2$ species should be obtainable that would be isoelectronic to the Group IV and Group VI (respectively) complexes. Thus it seemed that it should be possible to study the effect of net charge on the chemistry of this class of model compounds. This chapter details some of the approaches used to obtain $[Cp^*_2TaX_2]^{-/0/+}$ type complexes and attempts to demonstrate some of their reactivity patterns.

RESULTS AND DISCUSSION

Synthesis and characterization of $[Cp^*_2TaX_2]^{+/0/-}$ complexes. The reaction of $Cp^*_2TaCl_2$ (1) with methyl magnesium bromide (≥ 2 equivalents) in diethyl ether proceeds overnight (12 hours) at 25°C to yield maroon $Cp^*_2TaMe_2$ (2). This paramagnetic 17 electron complex is quite thermally stable (it can be sublimed at 140°C under high vacuum), much more so than Cp_2NbMe_2 which was found to explosively eliminate methane at 130°C.[3] Analytically pure **2** can be more conveniently obtained as maroon needles from slowly cooled petroleum ether solutions. The reaction proceeds similarly with $Cp^*CpTaCl_2$, **3**, to yield the mixed ring dimethyl complex **4**. The preparation of the normal ring Cp_2TaMe_2 via a similar route has been reported.[4] Reactions with other alkyl Grignards (RMgX; R = phenyl and benzyl) tended to give messy reactions that appeared (by mass spectrometry) to contain all possible permutations of $Cp^*_2Ta(R)(Cl)$, $Cp^*_2Ta(R)(X)$, $Cp^*_2Ta(X)(Cl)$, etc. and were not followed up.

The EPR spectra of **1** and **2** (Figure 1) show the expected 8 line patterns (^{181}Ta: I = 7/2, 99.99%). Note that complexes with halide ligands tend to show much broader patterns (larger hyperfine coupling, A_{iso}) than those without (Table 1). This has been observed previously and roughly corresponds with L-M-L angle, which is dependent both on ligand electronegativity and steric bulk.[5] Both **1** and **2** show fairly reversible ($\Delta E_p \approx$ 90-170 mv)[6] one electron electrochemical oxidations (Figure 2) at relatively low potentials. While **2** also undergoes a reversible reduction, **1** shows a completely irreversible wave. This observation is consistent with the chemical reduction of $(C_5R_5)_2MCl_2$ (R = H, Me; M = Nb, Ta) complexes to prepare derivatives containing the $(C_5R_5)_2MCl$ unit.[7]

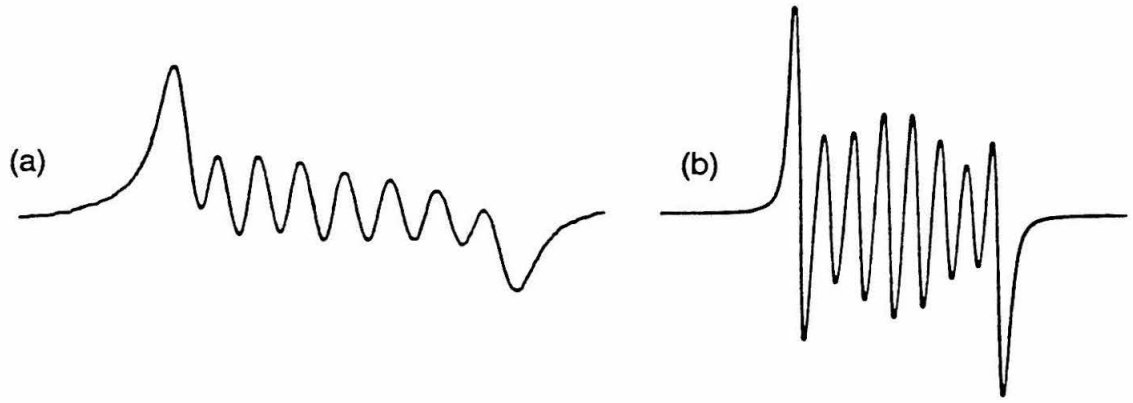


Figure 1. EPR spectra in toluene at 25°C: (a) $Cp^*_2TaCl_2$: g_{av} = 1.8970, A(Ta) ≈ 131 G. (b) $Cp^*_2TaMe_2$: g_{av} = 1.9856, A(Ta) = 79.5 G.

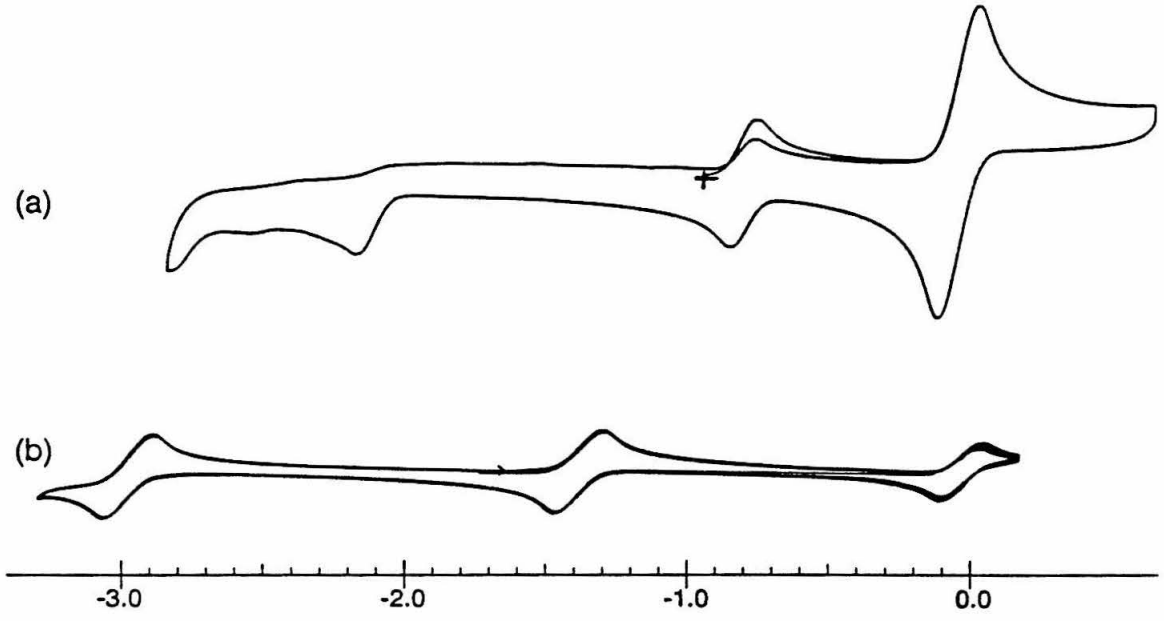


Figure 2. Cyclic voltammagrams in a conducting $TBABF_4$/toluene mixture[8] (air and water free) using a scan rate of 100 mV/s, silver wire electrodes, and internal ferrocene added as a reference (0.0 V): (a) $Cp^*_2TaCl_2$ ($E_{½}^{+/0}$ = -0.75 V; $E_{½}^{0/-}$ = -2.1 V). (b) $Cp^*_2TaMe_2$ ($E_{½}^{+/0}$ = -1.37 V; $E_{½}^{0/-}$ = -2.97 V).

Table 1. EPR data for niobocene and tantalocene complexes.

compound	solvent	g_{av}	$A_{iso}(M)/G$	ref
Cp_2NbCl_2	benzene/cyclopropane	1.977	116.5	a
Cp_2NbF_2	benzene/cyclopropane	2.01	115	b
Cp_2NbMe_2	benzene/cyclopropane	1.9984	88.8	a
Cp_2NbH_2	benzene/cyclopropane	2.0097	45.9 (A_H = 45.9)	a
$Cp^*_2NbCl_2$	benzene	2.01	N.R.	c
$Cp^*_2NbMe_2$	benzene	2.018	90	d
$Cp^*_2TaCl_2$	toluene	1.897	131	e
Cp'_2TaMe_2	benzene/cyclopropane	1.993	93	a
$Cp^*_2TaMe_2$	toluene	1.986	79.5	e
$Cp^*_2TaH_2$	dioxane	2.000	70	e
Cp_2TaH_2	benzene/cyclopropane	2.006	66	a, f

(a) Elson, I. H.; Kochi, J. K.; Klabunde, U.; Manzer, L. E.; Parshall, G. W.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 7374-6. (b) Sala-Pala, J.; Amaudrut, J.; Guerchais, J. E.; Mercier, R.; Douglade, J.; Theobald, J. G. *J. Organomet. Chem.* **1981**, *204*, 347-59 (c) Bell, R. A.; Cohen, S. A.; Doherty, N. M.; Threlkel, R. S.; Bercaw, J. E. *Organometallics* **1986**, *5*, 972-5. (d) Threlkel, R. S.; Bercaw, J. E. unpublished results. (e) this work. (f) no A_H splitting was observed due to broad linewidths.

Odd electron complexes **1-4** are readily oxidized by silver salts ($AgBF_4$, $AgCF_3SO_3$, *etc.*) in methylene chloride to provide 16 electron cationic species. These tend to be fluorescent yellow (dialkyls) to orange (dihalides) compounds that are very soluble in halogenated hydrocarbons but essentially insoluble in aromatic or ethereal solvents. These are diamagnetic d^0 compounds that can be considered charged analogues to the well studied Group IV metallocenes. In the NMR spectra (Table II), the Cp* resonances tend to come between δ 2-2.5, quite far downfield compared to neutral permethyltantalocene complexes that we have studied (*cf.* Chapter 2). It is interesting to note that the positions of these chemical shifts do not seem to be dependent on the identity of the counterion, consistent with our belief that these complexes exist as discrete ions in solution.

Due to the high stability and interesting chemistry of the dimethyl compounds, it was of interest to try to study the hydride complexes. The metallocene dihydrides have never been prepared for the Group V metals and have only been transiently observed at low temperature by EPR spectroscopy.[9] It seemed logical to start from the known hydride complex, $Cp^*_2TaH_3$. Attempts to abstract hydride from this compound with triphenylcarbenium ion did appear to lead to a cationic complex, although the reaction was somewhat messy and irreproducible. A much cleaner entry involved the protonation of $Cp^*_2TaH_3$ with $HBF_4 \cdot Et_2O$ in diethyl ether resulting in evolution of H_2 and precipitation of the cation as a yellow powder. Although the exact identity of this compound is still in question, it appears to have the general formula $[Cp^*_2TaH_2][BF_4]$, **5**. Reduction of **5** with potassium napthalenide affords deep maroon solutions, and black needles of this paramagnetic complex, **6**, can be obtained by crystallization from petroleum ether solutions. The room temperature EPR spectrum of **6** (Figure 3) is supportive of this assignment with relatively small hyperfine (A_{iso} = 70G) and possible some line broadening from the unresolved hydrogen coupling. Further reduction Na/K alloy in dioxane yields a diamagnetic red-brown solution, the NMR of which is consistent with an anionic dihydride complex (δ_{Cp^*} = 1.94 (s), δ_H = -9.90 (s)).

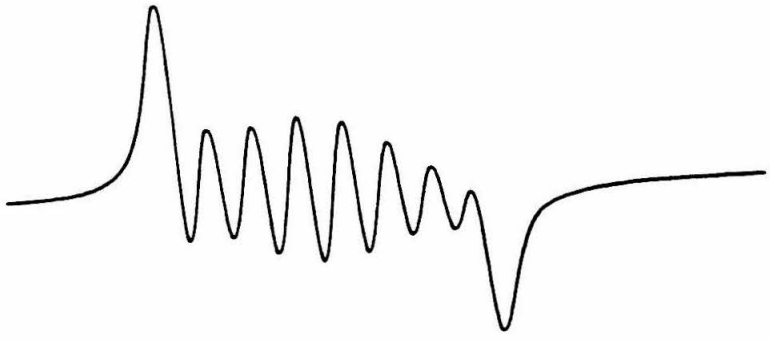
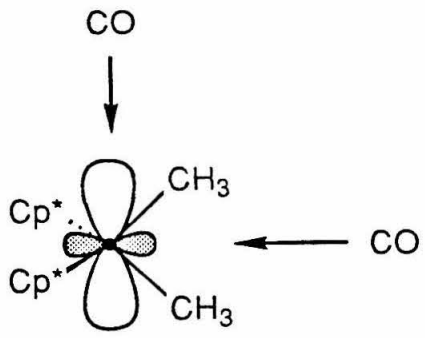


Figure 3. Room temperature EPR spectrum of $Cp^*_2TaH_2$ in dioxane: g_{av} = 2.000, $A_{iso} \approx$ 70G.

Reduction of **2** with Na/K alloy (Na is not strong enough a reductant alone) in THF affords a brick-red solution. Addition of petroleum ether leads to precipitation of black microcrystals of $[K][Cp^*_2Ta(CH_3)_2]$ (**7**). While we had hoped to compare the reactivity of such anionic 18 electron complexes to their neutral Group VI analogues, their chemistry is dominated by their potent reducing power. Thus reaction with CO and CO_2 leads instantly to reduction of the substrates and formation of paramagnetic $Cp^*_2TaMe_2$ and white precipitates. It is also difficult to monitor the chemistry of this complex by NMR spectroscopy unless there is added reducing agent. Typically it appears that a small amount tends to be oxidized to paramagnetic **2** leading to loss of the signals.

Chemistry of cationic $Cp^*_2TaX_2$ complexes. Oxidation of **1** and **2** can also be readily effected by agents other than silver salts. For instance by carefully monitoring (NMR spectroscopy) the reactions of **1** and **2** with oxygen, nitric oxide, and peroxides, the cations can be observed as the initially formed products. The dichloride cations undergo further chemistry to yield $Cp^*_2Ta(=O)Cl$[10] as the final product. Subsequent reactions of the dimethyl tend to be more messy, likely due to the reactive nature of the resulting anions (*e.g.* superoxide[11]). The cationic product derived from **2** and NO appears to undergo a series of reactions similar to that previously reported for the niobocene analogue[12] to finally yield $Cp^*_2Ta(=O)CH_3$ as the organometallic product. The reaction with oxygen ultimately results in several products including $Cp^*_2Ta(=CH_2)CH_3$ and methanol.

In spite of the fact that these are 16 electron compounds with an open coordination site, **3** and **4** exhibit very little reactivity with added ligands. For instance $[Cp^*_2TaMe_2][BF_4]$ (**8a**) reacts with CO only slowly over a two day period at 25°C to form a statistical (2:1) mixture of the two possible η^2-acyl complexes (**9a**: O-*exo*, **9b**: O-*endo*). In comparison, the reaction with CO in less sterically encumbered systems (Cp_2TaMe_2, $Cp^*CpTaMe_2$, and Cp_2ZrMe_2) occurs very rapidly to give only the thermodynamic product (O-*endo*).[13] Thus the observed mixture of acyl



isomers is quite interesting in that previous experimental results and theoretical calculations seemed to indicate a preferred direction of attack of incoming CO on the metallocene complex, followed by a rearrangement to the thermodynamically favored product. Heating the permethyltantalocene complexes to 50°C leads to a slow isomerization (k_{isom} = 2.1(1)x10^{-6} s^{-1}; $\Delta G^{\ddagger}$ = 27.3 kcal·mol^{-1}) to finally yield only the O-*endo* isomer. It seems that the isomerization process, which is likely a simple rotation about the Ta-COMe bond, is slowed by steric interactions with the two bulky pentamethylcyclopentadienyl ligands allowing both isomers to be observed at room temperature. The slow reaction even at 25°C may also indicate a steric effect on the initial CO addition reaction. It might be expected that this would favor addition at the central position of the wedge rather that the outside which seems to be preferred electronically. CO is a fairly small ligand however and the addition of the related π-acid methylisocyanide occurs rapidly to form a single iminoacyl product. Therefore the slow carbonyl addition reaction may simply be a concentration effect since a larger portion of the added CO would be expected to remain in the gas phase above the reaction solution.

No other insertion of other types of unsaturated ligands (alkenes, internal alkynes, CO_2, *etc.*) have been observed to occur up to the decomposition temperatures of the cationic alkyl complexes (*vide infra*). Terminal alkynes did appear to give some reaction competitive with decomposition of the starting material but these mixtures were difficult to characterize and were not followed up. The BF_4 salt of cationic hydride complex **6** was also observed to be unreactive

toward all of the substrates tried. There was concern, however, that the BF_4 anion might be able to interact with the less sterically encumbered $Cp^*_2TaH_2^+$ moiety. Thus the preparation of a cationic hydride complex with the more innocent counterion BPh_4 was attempted:

$$Cp^*_2TaH_3 + [Me_3NH][BPh_4] \xrightarrow[-Me_3N]{Me_2C=O} [Cp^*_2Ta(OCHMe_2)H][BPh_4]$$

$$Cp^*_2TaH_3 + [Me_3NH][BPh_4] \xrightarrow[-Me_3N]{N\equiv CMe} [Cp^*_2Ta(NH=CHMe)][BPh_4]$$

The products obtained in these reactions are consistent with the formation of a reactive form of $Cp^*_2TaH_2^+$ followed by an insertion reaction of a molecule of solvent. Attempts to prepare the hydride salt in less reactive solvents (methylene chloride and nitromethane) appeared to lead to several products possibly due to high reactivity of the species formed.

Acid-base chemistry and 1,2-elimination reactions of $[Cp^*_2Ta(CH_3)_2]^{-/+}$. As reported by Schrock[14] for $Cp_2TaMe_2^+$, complex **4** is deprotonated by a wide variety of bases (KH, RLi, $R_3P=CH_2$) to form $Cp^*_2Ta(=CH_2)CH_3$ (**10**) in high yield (70-90% isolated). **10** can also be protonated to regenerate **8**:

$$Cp^*_2Ta(CH_3)_2^+ \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} Cp^*_2Ta(=CH_2)CH_3$$

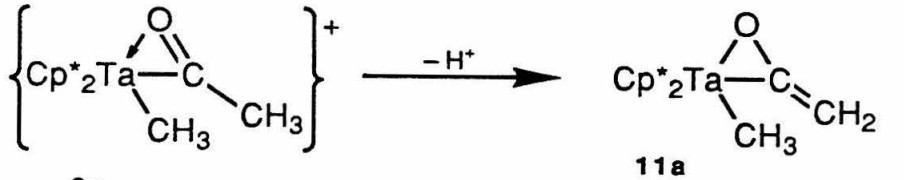
In fact, the deprotonation reaction provides a convenient pathway (Eq. 1) for the preparation of **10** from permethyltantalocene dichloride, since each step goes very cleanly and in high yield.

$$Cp^*_2TaCl_2 \xrightarrow[MeMgBr]{80\ \%} Cp^*_2Ta(CH_3)_2 \xrightarrow[AgBF_4]{95\ \%} Cp^*_2Ta(CH_3)_2^+$$

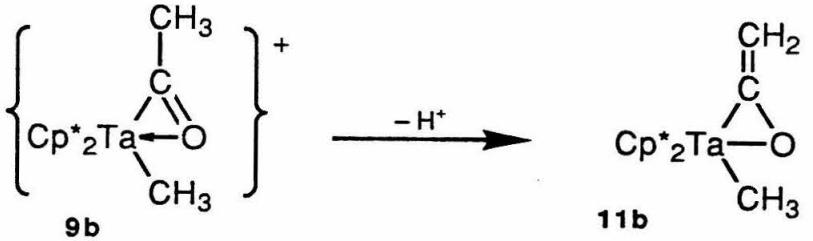
$$Cp^*_2Ta(CH_3)_2^+ \xrightarrow[-H^+]{80\ \%} Cp^*_2Ta(=CH_2)CH_3 \qquad (1)$$

10

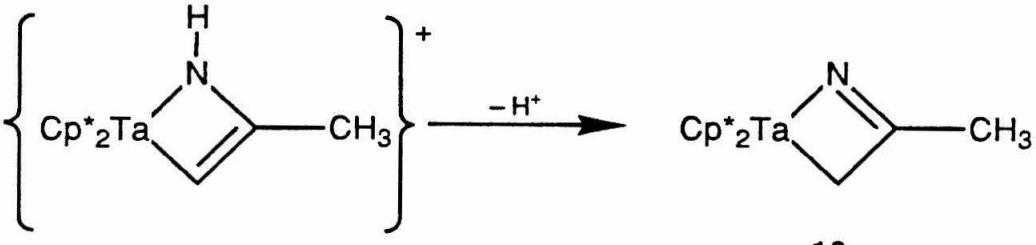
With the wide variety of $Cp^*_2Ta(=X)R$ complexes that have now been prepared and the large number of cationic complexes that may possibly be made, it should be possible to prepare a wide variety of new complexes *via* acid-base reactions. For example complexes such as the cationic acyls can be readily deprotonated to form the neutral tantalum ketene complexes **11a,b**. Neutral zirconocene acyls exhibit similar chemistry to yield anionic ketenes. The cationic nitrogen containing metallacycle, **12**, (*vide infra*) is deprotonated at nitrogen to form a neutral azametallacyclobutadiene complex, **13**. We have not attempted to try to reprotonate these compounds to see if the original cationic precursors are obtained.



9a **11a**



9b **11b**



12 **13**

It had been hoped that protonation of $Cp^*_2TaR_2^-$ complexes would lead to formation of $Cp^*_2TaR_2H$ compounds which might be expected to undergo facile reductive elimination of RH. Unexpectedly, the reaction of (**7**) with $HBF_4 \cdot Et_2O$ at room temperature proceeded with evolution of hydrogen and not methane gas and formation of $Cp^*_2Ta(=CH_2)Me$. This can either

occur *via* an initial protonation of the metal center to form the desired complex followed by a rapid "1,2-elimination" of H_2 or else by some direct abstraction of H^-. Experiments have not yet been performed to distinguish between these two possibilities.

Thermal decomposition of $Cp^*_2Ta(CH_3)_2^+$ complexes (**8a-c**) also appears to involve a 1,2-elimination pathway. Thermolysis of **8a-c** in chlorinated solvents was observed to proceed to the dichloride cations with loss of methane (1 equivalent as measured by Toepler for **8a**). Kinetic measurements confirmed a first order decomposition of **8a-c** that does not depend greatly on the nature of the counterions (Table III). Thermolysis of **8a** and **8a**-d_6 in $CDCl_3$ produced only CH_4 and CD_4, respectively. The rate does not appear to depend on the solvent as the rates in $CDCl_3$, $CDCl_2$, and CD_3CN are virtually identical. The final products did vary depending on the nature of the solvent (*vide infra*). The deuterium kinetic isotope effect (k_H/k_D) was found to be 3.5 (3) at 90°C in $CDCl_3$. Monitoring the kinetics over a range of temperatures of 39°C allowed the determination of the activation parameters for the 1,2-elimination of methane from **8a**: $\Delta H^{\ddagger}$ = 25.8(6) kcal · mol^{-1} and $\Delta S^{\ddagger}$ = -8.5(5) e.u..

Table III. Kinetic data for 1,2-elimination of methane from $[Cp^*_2Ta(CH_3)_2]^+$.

compound	solvent	T (°C)	k (s^{-1})	$\Delta G^{\ddagger}$ (kcal · mol^{-1})
8a	$CDCl_3$	78	$8.5(1)\times10^{-6}$	28.8(1)
		90	$3.4(2)\times10^{-5}$	28.8(1)
		104	$1.30(5)\times10^{-4}$	28.95(9)
		117	$3.6(1)\times10^{-4}$	29.2(1)
8a	CD_2Cl_2	90	$3.07(5)\times10^{-5}$	28.88(6)
8a	CD_3CN	78	$8.2(3)\times10^{-6}$	28.8(1)
8a-d_6	$CDCl_3$	90	$9.7(3)\times10^{-6}$	29.7(1)
8b	$CDCl_3$	108	$3.0(1)\times10^{-4}$	28.6(1)
8c	$CDCl_3$	90	$3.22(5)\times10^{-5}$	28.85(9)

These results are remarkably similar to those observed for the analogous decomposition of $Cp^*_2TiMe_2$.[16] This evidence suggests that the reaction is as in Eq. 2, with the intermediacy of a cationic tantalocene methylene moiety that is, unfortunately, too unstable to observe and reacts with the solvent to give the observed products.[17]

$$Cp^*_2Ta(CH_3)_2^+ \xrightarrow{-CH_4} [Cp^*_2Ta{=}CH_2^+] \xrightarrow{\text{solvent}} \text{products} \qquad (2)$$

Performing the thermolysis of **8** in acetonitrile instead of halogenated solvents leads to predominant formation of metallacycle **12** as the final product. This compound can be envisioned as deriving from acetonitrile addition to the methylene intermediate to initially give **14** (Eq. 3) followed by a 1,3-hydrogen shift to give **12**.

$$Cp^*_2Ta{=}CH_2^+ \xrightarrow{N{\equiv}CMe} [Cp^*_2Ta\text{-}CH_2\text{-}CMe{=}N]^+ \xrightarrow{1,3\text{-shift}} [Cp^*_2Ta\text{-}CH{=}CMe\text{-}NH]^+ \qquad (3)$$

Another Cp* containing species is observed in the NMR spectrum that could be some **14** as a minor side product. Similar types of rearrangements have been observed for some tantalum 5-membered ring analogues.[18] Attempts to trap the methylidene species with other solvents and ligands was unsuccessful. For example, the thermolysis carried out in acetone led only to paramagnetic products. If several equivalents of terminal alkyne was added to a chloroform solution of **2** and thermolyzed, several products other that $Cp^*_2TaCl_2^+$ were observed (but none were completely characterized). Perhaps if a sufficiently unreactive solvent and a reasonalbly large excess of ligand were used, it might be possible to form other products containing the $Cp^*_2Ta{=}CH_2$ fragment.

Table II. ^{1}H and ^{13}C NMR data for cationic and anionic tantalocene complexes.

Compound	Assignment	^{1}H δ/PPM (mult, J)	^{13}C δ/PPM (mult, J)
$[Cp^*_2Ta(Cl)_2][BF_4]$ **a-c**	η^5–$C_5(CH_3)_5$	2.39 (s)	129.6 (s) 12.1 (q, 129)
$[Cp^*CpTa(Cl)_2][BF_4]$ **a,d**	η^5–$C_5(CH_3)_5$ η^5–C_5H_5	2.49 (s) 6.75 (s)	
$[Cp^*_2TaH_2][BF_4]$ **a,c** **5**	η^5–$C_5(CH_3)_5$ Ta-H	2.30 (t, 1.4 Hz) 2.20 (s, br)	
$[Cp^*_2Ta(HN{=}CHCH_3)][B(C_6H_5)_4]$ **c,h**	η^5–$C_5(CH_3)_5$ N*H* C*H*CH_3 CH*CH*$_3$ B(C_6H_5)$_4$	1.88 (s) ≈6.9 (m) 7.67 (dq; 5.4, 5.3) 1.72 (d, 5.4) 7.4 (m, br) 7.02 (≈t, 7.4) 6.88 (t, 7.2)	
$[Cp^*_2Ta(OCH(CH_3)_2)H][B(C_6H_5)_4]$ **c,h**	η^5–$C_5(CH_3)_5$ Ta-*H* OC*H*$(CH_3)_2$ OCH(C*H*$_3)_2$ B(C_6H_5)$_4$	2.01 (s) 10.40 (s) 4.91 (septet, 6.1) 1.13 (d, 6.1) 7.4 (m, br) 7.0 (≈t, 7.4) 6.86 (t, 7.2)	
$[K][Cp^*_2Ta(CH_3)_2]$ **a,e** **7**	η^5–$C_5(CH_3)_5$ CH_3	1.58 (s) -2.00 (s)	
$[Cp^*_2Ta(CH_3)_2][BF_4]$ **a-c** **8a**	η^5–$C_5(CH_3)_5$ CH_3	2.10 (s) -0.21 (s)	122.1 (s) 11.6 (q, 128) 61.2 (q, 122)
$[Cp^*_2Ta(CH_3)_2][B(C_6H_5)_4]$ **a,cb** **8b**	η^5–$C_5(CH_3)_5$ CH_3 B(C_6H_5)$_4$	2. (s) -0.2 (s,br)	
$[Cp^*_2Ta(CH_3)_2][CF_3SO_3]$ **a,c** **8c**	η^5–$C_5(CH_3)_5$ CH_3	2.11 (s) -0.22 (s)	

Compound	Assignment	^1H δ/PPM (mult, J)	^{13}C δ/PPM (mult, J)
$[Cp^*CpTa(CH_3)_2][BF_4]$[a,f]	η^5–$C_5(CH_3)_5$	2.15 (s)	
	η^5–C_5H_5	6.30 (s)	
	CH_3	0.24 (s)	
$[Cp_2Ta(COCH_3)CH_3][BF_4]$[a,d]	η^5–C_5H_5	5.86 (s)	
	$COCH_3$	3.44 (s)	
O-*endo*	CH_3	0.89 (s)	
$[Cp^*CpTa(COCH_3)CH_3][BF_4]$[a,f]	η^5–$C_5(CH_3)_5$	1.91 (s)	115.5 (s)
			11.4 (q, 129)
	η^5–C_5H_5	5.67 (s)	108.3 (d,qn; 181,7)
O-*endo*	$COCH_3$	3.35 (s)	
	CH_3	0.53 (s)	29.4 (q, 131)
	$COCH_3$		236.2
$[Cp^*_2Ta(COCH_3)CH_3][BF_4]$[a,c]	η^5–$C_5(CH_3)_5$	1.86 (s)	
	$COCH_3$	2.99 (s)	
9a	CH_3	0.05 (s)	
$[Cp^*_2Ta(COCH_3)CH_3][BF_4]$[a,c]	η^5–$C_5(CH_3)_5$	1.88 (s)	
	$COCH_3$	3.17 (s)	
9b	CH_3	0.10 (s)	
$Cp^*_2Ta(\eta_2$-O=C=$CH_2)CH_3$[g,h]	η^5–$C_5(CH_3)_5$	1.59 (s)	
	O=C=CH_2	5.50 (s), 4.40 (s)	
11a	CH_3	0.0 (s)	
$Cp^*_2Ta(\eta_2$-O=C=$CH_2)CH_3$[g,h]	η^5–$C_5(CH_3)_5$	1.61 (s)	
	O=C=CH_2	5.69 (s), 4.07 (s)	
11b	CH_3	-0.04 (s)	
$[Cp^*_2$Ta-NHC(CH_3)=CH$][BF_4]$[a,b,d]	η^5–$C_5(CH_3)_5$	1.87 (s)	123.3 (s)
			11.4 (q, 128)
	CH_3	1.8-2.0	24.5 (q)
12	=*CH*-Ta	4.38 (s)	94.3 (d, 163)
	-NH*C*(CH_3)=CH-		167.4 (s)
	N-*H*	5.8 (s, br)	
Cp^*_2Ta=NC(CH_3)=CH[g,h]	η^5–$C_5(CH_3)_5$	1.79 (s)	
	CH_3	1.91 (s)	
14	=*CH*-Ta	5.10 (s)	

(a) ^1H spectrum measured on a JEOL FX-90Q spectrometer. (b) ^{13}C spectrum measured on a JEOL GX-400 spectrometer. (c) Measured in $CDCl_3$. (d) Measured in CD_3CN. (e) Measured in d_8-THF. (f) Measured in $CDCl_2$ (g) Measured in C_6D_6. (h) Measured on a Bruker AM-500 spectrometer.

EXPERIMENTAL

General Considerations. All air sensitive manipulations were carried out using glove box or high vacuum line techniques. Hydrocarbon and ethereal solvents were dried over CaH_2 and stored over titanocene or sodium benzophenone (respectively). Benzene-d_6 and toluene-d_8 were dried over activated 4 Å molecular sieves and stored over titanocene. $CDCl_3$, CD_2Cl_2, and CH_2Cl_2 were vacuum transferred from CaH_2. Other deuterated solvents along with acetone and acetonitrile were dried and stored over molecular sieves. Argon was purified by passage over MnO on vermiculite and activated molecular sieves.

NMR Spectra were recorded on Varian EM-390 (^1H, 90 MHz), JEOL FX90Q (^1H, 89.56 MHz; ^{13}C, 22.50 MHz; ^{19}F, MHz), JEOL GX400Q (^1H, 399.78 MHz; ^{13}C, 100.38 MHz) and Bruker AM500 (^1H, 500.13 MHz) spectrometers. Infrared spectra were recorded on a Beckman 4240 spectrometer and peak positions are reported in cm^{-1}. Mass spectra and elemental analyses were conducted by L. Henling or F. Harvey of the Caltech Analytical Laboratory.

Starting materials. Diethyl ether solutions of CH_3MgBr and CD_3MgBr were obtained from Aldrich. $Cp^*_2TaCl_2$ (**1**), $Cp^*CpTaCl_2$ (**3**), and $Cp^*_2TaH_3$ were prepared as previously described.[19] $[Cp_2Ta(CH_3)_2][BF_4]$ was prepared as described by Schrock.[14] Silver salts were purchased from Aldrich except for $AgBPh_4$ which was prepared by the reaction of $AgNO_3$ with $NaBPh_4$.

$Cp^*_2Ta(CH_3)_2$ (2). A diethyl ether solution of CH_3MgBr (2.9 M, 8 mL, 23 mmole) was added to a solution of **1** (5.4 g, 10.2 mmole) in diethyl ether at -78°C. This mixture was allowed to warm to room temperature and stirred for 24 hrs, resulting in a maroon solution. The ether was removed and the product extracted into petroleum ether and slowly cooled to -78°C to produce maroon needles (4.0 g, 81% yield). Infrared (C_6D_6, CaF_2): 2980, 2945, 2902, 2825, 1489, 1441, 1380. Mass spectrum (m/e): 481 (M^+), 466, 450. Anal. Calcd. for $C_{22}H_{36}Ta$: C, 54.89; H, 7.48. Found: C, 54.89; H, 7.53. EPR (toluene): g = 1.9856, A_{iso} = 79.5 G.

$Cp^*CpTa(CH_3)_2$ (4). Prepared as for **2** above with 580 mg (1.3 mmole) of $Cp^*CpTaCl_2$ and 1.2 mL CH_3MgBr/Et_2O (2.9 M, 3.5 mmole) in approximately 30 mL of diethyl ether. Extraction and crystallization from petroleum ether gave 400 mg (76% yield) of maroon solid.

$[Cp^*_2TaH_2][BF_4]$ (5). Liquid $HBF_4 \cdot Me_2O$ was added to a solution of $Cp^*_2TaH_3$ (1.01 g, 2.2 mmole) in 15 mL diethyl ether at about -20°C until addition no longer led to gas evolution (adding too much acid will lead to an oily layer). This resulted in a pale yellow solution and yellow precipitate which was filtered off and washed 3 times with ether. This solid was dried *in vacuo* to yield 1.2 g (100% yield) of yellow microstalline **5.** ^{19}F NMR ($CDCl_3$): $\delta(B\underline{F}_4)$ = 8.1 (m).

$Cp^*_2TaH_2$ (6). A mixture of **5** (286 mg, 0.53 mmole) and potassium napthalenide (108 mg, 0.64 mmole) were weighed into a flask and 15 mL of diethyl ether added at -78°C. As this yellow slurry was allowed to warm to room temperature a red color developed and white precipitate formed. The solvent was removed *in vacuo* after 1 hour and the resulting solid extracted into petroleum, filtered, and concentrated. Slow cooling to -78°C gave 108 mg (45% yield) of black needles. Infrared (nujol): 1760 (m, br), 1640 (w, br), 1022 (m).

$[Cp^*_2Ta(OCH(CH_3)_2)H][BPh_4]$. A suspension of $Cp^*_2TaH_3$ (203 mg, 0.45 mmole) and $[Me_3NH][BPh_4]$ (178 mg, 0.47 mmole) was stirred at room temperature in 15 mL of acetone resulting in gas evolution and a yellow coloration. After one hour, the solvent was removed and the resulting yellow and white solids extracted into methylene chloride. This yellow solution was filtered and concentrated. Addition of diethyl ether led to precipitation of 340 mg (98% yield) of yellow powder. Anal. Calcd. for $C_{47}H_{58}OTaB$: C, 67.95; H, 7.04. Found: C, 67.96; H, 6.86.

$[Cp^*_2Ta(NH{=}CHMe)][BPh_4]$. A suspension of $Cp^*_2TaH_3$ (105 mg, 0.23 mmole) and $[Me_3NH][BPh_4]$ (93 mg, 0.25 mmole) was stirred at room temperature in 10 mL of acetonitrile resulting in gas evolution and a clear solution. After one hour, the solvent was removed and the resulting oily white solid extracted into methylene chloride. This solution was filtered and concentrated. Addition of diethyl ether led to precipitation of 167 mg (94% yield) of white

powder. Anal. Calcd. for $C_{46}H_{55}NTaB$: C, 67.74; H, 6.68; N, 2.15. Found: C, 67.90; H, 6.81; N, 1.72.

[K][Cp*$_2$Ta(CH$_3$)$_2$] (7). A mixture of **2** (544 mg, 1.13 mmole) and Na/K (59 mg, 1.25 mmole) alloy were stirred for one day at room temperature in 20 mL of THF resulting in a thick red solution which was filtered and concentrated. Addition of petroleum ether resulted in precipitation of black microcrystals (338 mg, 57% yield).

[Cp*$_2$TaCl$_2$][BF$_4$]. A solution of **1** (794 mg, 1.5 mmole) and $AgBF_4$ (306 mg, 1.6 mmole) in 15 mL of methylene chloride was stirred for 2 hrs at room temperature resulting in bright orange solution. This solution was filtered through a fine porosity sintered glass frit to remove Ag^0 and concentrated to 3 mL. Addition of diethyl ether at -78°C afforded 893 mg (96% yield) of orange crystalline solid. ^{19}F NMR ($CDCl_3$): $\delta(B\underline{F}_4)$ = 8.1 (m).

[Cp*$_2$Ta(CH$_3$)$_2$][BF$_4$] (8a). A solution of **2** (1.0 g, 2.1 mmole) and $AgBF_4$ (0.43 g, 2.2 mmole) in 15 mL of methylene chloride was stirred for 2 hrs at room temperature resulting in a yellow solution. This solution was filtered through a fine porosity sintered glass frit to remove Ag^0 and concentrated to 3 mL. Addition of diethyl ether at -78°C afforded 1.13 g (95% yield) of yellow crystalline **8a**. Anal. Calcd. for $C_{22}H_{36}TaBF_4$: C, 46.50; H, 6.39. Found: C, 46.29; H, 6.27. ^{19}F NMR ($CDCl_3$): $\delta(B\underline{F}_4)$ = 8.1 (m).

[Cp*$_2$Ta(CH$_3$)$_2$][B(C$_6$H$_5$)$_4$] (8b). Performed as for **8a** above with **2** (200 mg, 0.42 mmole) and $AgBPh_4$ (200 mg, 0.47 mmole) to yield 280 mg (84% yield) of yellow crystalline solid.

[Cp*$_2$Ta(CH$_3$)$_2$][CF$_3$SO$_3$] (8c). Performed as for **8a** above with **2** (360 mg, 0.75 mmole) and $AgCF_3SO_3$ (200 mg, 0.78 mmole) to yield 360 mg (76% yield) of yellow crystalline solid. ^{19}F NMR ($CDCl_3$): $\delta(C\underline{F}_3SO_3)$ = 83.8 (s).

[Cp*CpTa(CH$_3$)$_2$][BF$_4$]. Performed as for **8a** above with **4** (252 mg, 0.61 mmole) and AgBF$_4$ (121 mg, 0.62 mmole) to result in 265 mg (87% yield) of lemon-yellow microcrystalline solid.

[Cp*$_2$Ta(COCH$_3$)CH$_3$][BF$_4$] (9a,b). A solution of **8a** (450 mg, 0.79 mmole) in methylene chloride was stirred under roughly 2 atm CO in a glass bomb for two days at room temperature. Filtration of the resulting yellow solution followed by addition of diethyl ether lead to precipitation of 439 mg (93% yield) of a lemon-yellow microcrystalline mixture of the O-*endo* and O-*exo* cationic acyl isomers. Anal. Calcd. for $C_{23}H_{36}OTaBF_4$: C, 46.33; H, 6.09. Found: C, 45.89; H, 5.93.

Cp*$_2$Ta(=CH$_2$)CH$_3$ (10). THF was vacuum transferred onto a mixture of [Cp*$_2$TaMe$_2$][BF$_4$] (221 mg, 0.39 mmole)and KH (32 mg, 0.8 mmole) at -78°C. This suspension was allowed to stir and warm to room temperature resulting in an orange solution. After reacting overnight, the solvent was removed *in vacuo* and the crude product extracted into and crystallized from petroleum ether. This provided 137 mg (73% yield) of tan microcrystalline solid.

[Cp*$_2$Ta-NHC(CH$_3$)=CH][BF$_4$] (12). A solution of **4a** (214 mg, 0.38 mmole) in 5 mL of acetonitrile was thermolyzed in a glass bomb at 110°C for 4 days. The resulting deep red solution was filtered from an orange solid and pumped to dryness. This residue was extracted into methylene chloride, filtered, and 150 mg (67% yield) of a maroon microcrystalline solid precipitated by addition of diethyl ether. Infrared (nujol): 3300, 1591, 1487, 1307, 1060 (s,br), 1120, 712.

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